CO2 STORAGE AS CARBONATE MINERALS

Report Number PH3/17
February 2000

This document has been prepared for the Executive Committee of the Programme.
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Title: **CO_2 storage as carbonate minerals**
Reference number: **PH3/17**
Date issued: **February 2000**

Other remarks:

Introduction

This study is an assessment of above-ground processes that would bind CO_2 as a mineral carbonate. For example, a number of people have suggested converting naturally occurring mineral oxides to carbonates by reaction with CO_2 captured at a power station. The mineral carbonate would be stored indefinitely.

If carbonate storage were to be used, it could be a safe store for CO_2 captured during the generation of power from fossil fuels. Such a process would have the attraction of 'locking-up' CO_2 in a chemical that occurs naturally and is widely distributed, thus avoiding many of the environmental and safety concerns expressed about other storage options.

Potentially suitable minerals for CO_2 sequestration are, in general, complex silicates that originated deep within the earth's mantle. There are huge quantities of such rocks and, over geological time-scales, they naturally 'weather' to a carbonate by reaction with atmospheric CO_2. However, the carbonation reaction is extremely slow at normal temperatures and pressures. In addition, the mass of rock required is several times the mass of CO_2 stored. In principle, these disadvantages could be minimised by use of large-scale processes similar to those used in mineral extraction industries where large quantities of materials are routinely processed to recover a relatively small quantity of product.

The scientific basis for processes in which CO_2 is stored in carbonate minerals is assessed in the study. The practical implications are also assessed. Storage opportunities based on carbonate minerals are identified and their potential application described. Six potential processing routes are identified and assessed in outline. A 'favoured' option is selected for detailed evaluation.

The overall objective of this study is to assess the potential of mineral carbonates as a long-term store for fossil fuel derived CO_2, and to calibrate this against other CO_2 storage options.

Approach adopted

The study was done in several stages. Initially, an extensive literature review was undertaken to identify and classify processes suggested as being applicable to the sequestration of CO_2 as a mineral carbonate. The next stage in the study was a geological survey of the availability and type of potential source rocks. This was followed by a scientific critique of the required reactions.

Following the above, a short-list of potential process routes was prepared. Processes on the short-list were assessed in outline with the objective of identifying a 'favoured' process thought most likely to have potential as a sequestration option. This outline assessment was done using similar principles to the assessment methodology developed to assess novel power generation systems (see report PH3/16). The process were evaluated in terms of their ability to sequester the 3 million tonnes per year of CO_2 emitted from a modern coal-fired power station capable of producing $500MW_e$.

Two processes were assessed in detail. It was evident from the outline assessment that most of the processes were unlikely to be viable. One process was selected as being more likely to be viable than the others, but key thermodynamic factors that determine the design data for this process are not well documented or are not known. Therefore a better understood process known to have major drawbacks, but with much in common with the favoured process, was also selected for detailed examination; this process was used as a baseline for the assumptions necessary to evaluate the favoured process.

The study was undertaken by CSMA Consultants, of Redruth, Cornwall, England.

Results and discussion

Mineral carbonates can be formed from a variety of common minerals. Magnesium carbonate is the most commonly suggested carbonate to sequester CO_2 because it is stable and suitable source rocks are widely available (see section 2 of the main report). Magnesium is generally favoured over calcium as the metallic cation because magnesium-rich rocks contain more reactive material per tonne than their calcium equivalents.

On a geological time-scale these oxides and carbonates are not stable. Weathering and erosion slowly convert exposed mineral oxides into carbonates by absorbing atmospheric CO_2, the carbonates slowly form sedimentary deposits, over aeons the sedimentary deposits enter the earth’s mantle, and the carbon is eventually recirculated as CO_2 emission from volcanic activity. However, this geological cycle does not invalidate sequestration of anthropogenic CO_2 as a mineral carbonate because the quantities and timescale required are orders of magnitude smaller.

There is a concern that mineral carbonates are sparingly soluble in rain water which, even if unaffected by sulphur and nitrogen oxides, is mildly acidic. The susceptibility and rate of dissolution of the sequestration product would depend on its form and would need to be tested. It is possible that storage areas would need to be sealed to prevent water ingress.

initial screening

Table S1 lists the processing options identified in a literature review. Each process is described in section 5 of the report where the processes are assessed in outline to determine their likely viability. As can be seen in table S1, many of the processes are similar to each other in relying on the formation of a hydroxide which is reacted with CO_2 to produce a carbonate. This is because the thermodynamic equilibrium of most of these reactions is favoured by low temperatures - the high temperatures that are often necessary to get an adequate rate of reaction drive the equilibrium in the wrong direction. The chemistry is explained in section 4 of the main report. The equilibrium for the carbonation reaction with the hydroxide is relatively insensitive to temperature, therefore the reaction can be speeded up to viable rates by heating.

Table S1: Processes considered.

Process No.	Raw Material	Raw material reacts with:	CO_2 reacts with:	CO_2 stored as:
1	Mg silicate rock	HCl	$Mg(OH)_2$	$MgCO_3$
2	Mg-rich brine deposit	H_2O	$Mg(OH)_2$	$MgCO_3$
3a	Mg silicate rock	$MgCl_2$	$Mg(OH)_2$	$MgCO_3$
3b	Mg silicate rock	CO_2	$Mg_3Si_2O_5(OH)_4$	$MgCO_3$
4	Ca silicate rock	HCl	$Ca(OH)_2$	$CaCO_3$
5	$MgCO_3$ + NaCl	CO_2	$MgCO_3$ + NaCl	$NaHCO_3$

A brief outline of each process follows.

process 1

In process 1 a magnesium silicate rock is dissolved in hydrochloric acid (HCl); magnesium hydroxide is produced via intermediate stages in which H_2O and HCl are evaporated; the $Mg(OH)_2$ which is a fine powder reacts with CO_2 to form magnesium carbonate ($MgCO_3$). This process uses a widely available feedstock and standard technology and does not have any major unassailable environmental problems. This process is evaluated in depth in the report (see section 7) because it is well documented and represents a marker for the other potential mineral carbonate sequestration approaches. It is not viable as a CO_2 sequestration option. As demonstrated in the body of the report the dehydration and crystallisation stages of the process require more than 4 times the energy generated by the power station producing the CO_2. Overall the process produces more CO_2 than it sequesters.

process 2

The process relies on a naturally occurring Mg-rich brine; such brines are found in large continental evaporitic basins but are rare. The processing route is a modification of process 1, also involving an energy-intensive dehydration step. Huge volumes of hydrochloric acid are generated and have to be disposed of. This process is rejected as being unlikely to be viable or gain wide acceptance.

process 3a

In an effort to avoid the energy-intensive dehydration stage of processes 1 and 2 it has been proposed that a magnesium chloride melt could be used as a solvent for the synthesis of $Mg(OH)_2$. The process still requires a major dehydration step equivalent to about half the amount of evaporation in process 1. The net CO_2 savings of the overall process are likely to be small.

process 3b

This method attempts to avoid the energy-intensive steps of the above processes by direct carbonation. Although the method is kinetically unproven it was decided that it was likely to be the most attractive of the processing options identified and was therefore examined in detail (see later).

process 4

This process uses a calcium silicate rock which is dissolved in hydrochloric acid. The calcium hydroxide produced is dissolved in water and then reacted with CO_2 to produce calcium carbonate. Hugh volumes of water are involved as the solubility of $Ca(OH)_2$ is very low; the tailings lagoons required by the process would be enormous. Further, the concentration of Ca in silicate rocks is generally considerably lower than for Mg thus requiring more feedstock for a given sequestration capability. The process was deemed unsuitable for further investigation.

process 5

This process is based on the dissolution of $MgCO_3$ from dolomite.[1] There is a net sequestration of CO_2 because for every mole of $MgCO_3$ reacted there are two moles of sodium bicarbonate ($NaHCO_3$) produced. The basic chemistry and thermodynamics involved are proven. Extremely large quantities of material are involved; for example, the quantity of solids entering the reaction stage is about 8 times as large as for the equivalent step in process 1. The process would need to be located near the sea and an additional source of large quantities of salt (NaCl). In principle the $NaHCO_3$ could be stored dry but it is quite soluble in water and care would be needed to ensure that is did not find its way back into the

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[1] Dolomite is a mixture of calcium carbonate (54%) and magnesium carbonate (46%).

sea thus nullifying the CO_2 sequestration.[2] This factor in combination with the huge volumes of material to be handled make the process unattractive.

In summary, of the processes identified, those based on the use of magnesium silicate rock were deemed to have the most potential. The size of the plant to sequester the 3 million tonnes per year of CO_2 produced by a modern coal-fired power station of 500MWe capacity is not a problem. The tonnages involved with mining, primary processing, and final product storage are well within the production levels experienced by many mining operations. The main problem with the processes which rely on producing $Mg(OH)_2$ to react with CO_2 is that an energy-intensive evaporation step is required which can negate the net balance of CO_2 sequestration. Process 3b goes some way to avoiding this problem by the direct carbonation of magnesium in a $MgCl_2$ melt. It was therefore decided that this process would be examined in detail.

detailed assessment of the most favoured process (3b)

This process relies on the direct carbonation of dissolved magnesium silicate rock in a melt of $MgCl_2$. It avoids the energy-intensive dehydration and crystallisation steps which negate the potential for CO_2 sequestration of those processes making use of $Mg(OH)_2$. The process is illustrated in figure S1 below, section 8 of the main report contains the detailed assessment. (Throughout the assessment various assumptions made are referenced to process 1 as this process is much better defined; for this reason process 1 was also assessed in detail. See section 7 of the main report.)

A problem with magnesium-based processes for CO_2 sequestration that avoid formation of $Mg(OH)_2$ is that the carbonation relies on the equilibrium of the following reaction:

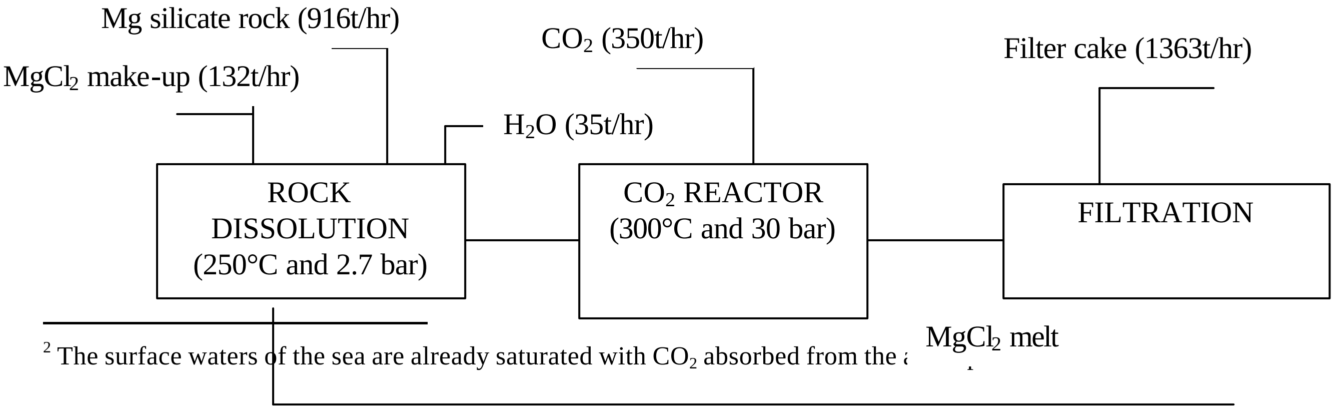
$$Mg^{++} + CO_2 + H_2O \quad MgCO_3 + 2H^+$$

The equilibrium of this reaction is very far in favour of the reactants (i.e. to the left) except when the pressure of CO_2 is high; hence considerable pressure is required to obtain adequate yields of $MgCO_3$.

The kinetics (i.e. speed) of the reactions involved in the process are not known. In the absence of this information reaction residence times deemed reasonably favourable were assumed, i.e. 15 minutes for the rock dissolution and 1 hour for the CO_2 sequestration. However, in practice, the reactions could be too slow to be of commercial interest.

It is not clear what material of construction would be used to contain the reactants, for the purposes of this study it is assumed the $MgCl_2$ melt and reactants could be handled using suitable corrosion resistant metal alloys and/or refractory materials.

Figure S1: Sketch of process 3b - direct carbonation in a melt of $MgCl_2$.



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[2] The surface waters of the sea are already saturated with CO_2 absorbed from the

In theory the process is essentially energy neutral with energy requirements being balanced by the exothermic carbonation reaction. In practice there will be a considerable energy demand; in the design case the demand was calculated to be 149MW i.e. about 30% of the 500MW output from the power station that produces the CO_2 sequestered. This figure makes no allowance for the energy used in production of the make-up $MgCl_2$ required to replace processing losses.

It is estimated that the loss of $MgCl_2$, mainly in the filter cake, would be equivalent to 2.5% of the total mass of the melt. The make-up could be imported but the quantity required would be a significant fraction of current world production. On site production of $MgCl_2$ from HCl and additional rock may be a preferred option, an initial evaluation showed that this would probably be financially beneficial.

Assuming on-site production of $MgCl_2$ the cost of CO_2 sequestration is calculated to be 62 \$/tCO_2 at a 10% discount rate. The capital cost of the mining and processing plant is estimated to be 420 \$million. The cost of make-up chemicals, mainly HCl, accounts for about a third of the total sequestration cost (22 \$/tCO_2). If $MgCl_2$ is imported the cost of sequestration at a 10% discount rate was calculated to be 80 \$/tCO_2. As a cross-check, the cost of sequestration using the better-understood process 1 was also derived; in this case the cost of sequestration is >200 \$/tCO_2.

It is possible that the design case could be improved by:

(i) installation of extensive heat recovery equipment to recover heat of reaction and use it for process heating.
(ii) reducing the requirement for make-up $MgCl_2$ by using a recovery process based on multi-stage counter-current decantation.

As can be seen in the sensitivity analysis, summarised in table S2 (section 8 of the report), the sequestration cost is insensitive to assumptions about the fuel and power consumption. However, if the losses of melt could be reduced by a factor of 4, i.e. to only about 0.6% of the circulating load, the cost of sequestration could be brought down to 46 \$/tCO_2.

Table S2: Sensitivity of sequestration cost \$/tCO_2 to changes in main variables: process 3b. (10% discount rate, on-site production of $MgCl_2$)

	Sequestration cost (\$/tCO_2)		
Value of parameter (relative to design case) **Variable**	**25%**	**100% (design case)**	**150%**
Capital cost	42	62	85
Make-up chemical requirement	46	62	73
fuel consumption	61	62	64
power consumption	61	62	63

A significant problem with this process is that a commercial supply of $MgCl_2$ in the quantities required is likely to be unrealistic. If on-site production from HCl is assumed this still requires extremely large volumes to be supplied which may render the process untenable.

It is demonstrated in the body of the report that process1, based on carbonation of $Mg(OH)_2$, requires more than 4 times the energy produced by the power station producing the CO_2, i.e. overall the process produces more CO_2 than it sequesters. The process of direct carbonation in a $MgCl_2$ melt appears to largely avoid this problem but considerable quantities of either $MgCl_2$ or HCl must be imported. Although the energy involved in manufacture of this material has not been accounted for in the study calculations, it is estimated that, in the case where $MgCl_2$ is imported, even the on-site processing has an energy requirement equivalent to about 30% of the output from the base-case power station. It is therefore likely that the estimated cost per tonne of net CO_2 sequestration would increase considerably if the full-cycle emissions are included.

Table S3 compares a number of sequestration options. It should be noted that the cost of CO_2 capture has to be added to the cost of storage to arrive at the overall cost of abatement. On the positive side, the potential for terrestrial storage of CO_2 as a mineral carbonate is virtually unlimited and the environmental issues it raises are relatively minor. However, the cost is likely to be a factor of ten greater than for most other sequestration options that are being considered, and considerable R,D &D would be required to prove its viability.

In summary, the mineral processing aspects of process 3b are not likely to be a problem, the size is well within current practice and the costs are not prohibitive. The rock dissolution and CO_2 sequestration processes are more problematic - even if the (unknown) kinetics are favourable, the cost of sequestration is likely to be considerably greater than alternative, better understood, methods of CO_2 sequestration. There are possibilities that the process design assumed in this study can be improved to reduce the cost of sequestration below 60$/t$CO_2$ but it is not likely that any such improvements could generate sequestration costs of <10$/t$CO_2$ as is achievable with other sequestration options.

As an alternative to processing the Mg-rich rock to sequester CO_2, it is suggested in the report that consideration be given to the following two possibilities:

(i) Selection of a suitable underground store for CO_2 sequestration on the basis of the rock strata's ability to react with the injected CO_2 to form stable carbonates. This would be an alternative underground storage approach to those listed in table S3 based on saline reservoirs and fossil fuel depositions. This approach would avoid concerns about very slow reactions and the costly above-ground processing required. This 'mineral trapping' mechanism, along with hydrodynamic trapping, is commonly discussed as one of the potential means by which CO_2 could be sequestered underground. The difference suggested here is that suitable sites might be selected primarily on the basis of the ability of CO_2 to react with the host rock. Such an approach would probably require the use of rock fracturing and other porosity enhancement techniques. It is possible that injection procedures, including perhaps the addition of chemical agents, could be optimised to encourage/promote the sequestration reaction.

(ii) There are naturally-occurring examples of microalgae acting as catalysts for the precipitation of magnesium carbonates; the CO_2 being obtained directly from the atmosphere. The prospects for industrial application of this process are probably slight but some researchers may think it worth investigation.

Expert Group comments

The draft report was circulated for expert review. Various comments on the details of the study have been dealt with in the final report.

One reviewer noted that, although not common, Mg and Ca hydroxides do occur naturally, so there may be niche applications where the CO_2 sequestration reaction could be used directly.

It was also noted that although rock and mineral compositions are often represented in terms of their oxide equivalents this can be misleading because the Ca and Mg are locked up in a silicate or aluminosilicate framework.

A Canadian reviewer noted the unique set of favourable circumstances in Saskatchewan with high Ca-Mg brines, open-pit coal mines, and the presence of surface clays to use as acid buffers.

One set of reviewers were strongly of the opinion that the make-up and heat recovery obstacles to the process based on a $MgCl_2$ melt (process3b) could be easily overcome. They suggest that the chloride content of the filter cake can be easily reduced by multistage countercurrent processing thus considerably reducing the cost of sequestration. They also suggest that heat can easily be recovered from the products by transferring most of it to the reactants; they proposed that, if successful, this would reduce costs and ease concerns about the overall net CO_2 sequestered.

Major conclusions

Of the sequestration processes identified only direct carbonation in a $MgCl_2$ melt appeared to have possible potential, the others are either impractical or consume energy on a scale large enough to negate any potential for CO_2 sequestration.

Sequestration of CO_2 in a mineral carbonate does have the potential advantages of being widely applicable and avoiding the possibility of accidental large-scale release. The environmental implications are likely to be relatively minor and surmountable.

R&D is required to establish basic information on the reactions involved in direct carbonation in a magnesium chloride melt. Suitable materials of construction for the processing equipment could be a significant problem.

The cost of sequestration, calculated to be 60\$/tCO_2 is considerably greater than for alternative options such as storage in a deep saline aquifer; it is unlikely that the cost could be brought down to a level at which it would be competitive with these other, more established options.

Recommendations

The sequestration of CO_2 as a mineral carbonate is an expensive option which is far from being established technology and its overall effectiveness would need validation before its use could be recommended. Given that other storage options, particularly those based on underground storage are rapidly gaining acceptability there is little incentive for IEA GHG to seek further development of this option. It is recommended that IEA GHG take no further action on above-ground processes aimed at sequestration of CO_2 in minerals.

Based on the chemistry examined in this report, selection of underground sites on the basis of their ability to sequester CO_2 by reaction underground with mineral oxides could be an interesting approach. Slow reactions would not be a major problem and it would avoid the high cost associated with above-ground processing. This approach would have the advantage of 'locking-up' the CO_2 i.e. it would minimise the concerns expressed about other underground storage methods (in which CO_2 is stored as a fluid) that there is a potential for accidental large-scale releases. It is recommended that IEA GHG evaluate this approach.

Table S3 *A comparison of options for sequestration of captured CO_2*[3]

Storage option	**Potential magnitude (Gt CO_2)**	**Availability and applicability**	**Environmental and safety issues**	**Illustrative storage cost US\$/tCO_2 (not including transport)**
1) Ocean:				
deep ocean	> 4000	proximity to deep ocean required; significant R&D requirement; questions about duration of storage; concerns about legality.	(i) dispersion options: local environmental issues. (ii) bulk store: accidental release and local environmental issues.	1-5
2) Underground:				
deep saline reservoirs	>800	widely distributed; existing off-shore application being monitored.	integrity of store has to be demonstrated – concern about potential hazard from rapid release or slow leakage.	1-2
disused gas fields	800	localised; largely based on existing technology.	if original seal is sound, relatively minor concerns about rapid release or slow leakage.	2-3
enhanced oil recovery/disused oil fields	130	localised; uses existing technology.	relatively minor leakage concerns	can be a net benefit
unminable coal seams	>15	regional availability. development of existing technology required.	relatively minor leakage concerns.	can be a net benefit but costs escalate rapidly above 20 GtCO_2
3) Terrestrial:				
mineral carbonates	large – potential not estimated	widely applicable; R&D on sequestration reactions required.	relatively minor concerns	60-100
bulk storage of CO_2	large in principle but constrained by cost	little restriction; existing technology can be used.	concern about potential for accidental release.	160

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[3] The overall cost of capture and sequestration should include the cost of capture, pressurisation, and transport. Typically, from a natural gas-fired power plant, for a transport distance of up to 1000 km, about 45\$/tCO_2 should be added to the figures in the table to arrive at the overall cost.

Client:
IEA Greenhouse Gas R&D Programme

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29 November 1999

Ref: 61-0156

I/R: MM/002

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CO_2 STORAGE AS CARBONATE MINERALS

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CO_2 STORAGE AS CARBONATE MINERALS

EXECUTIVE SUMMARY

CSMA Consultants Limited was commissioned by IEA Greenhouse Gas R&D Programme to investigate the potential of sequestering CO_2 within stable mineral carbonates. The study involved extensive literature research in combination with a scientific approach to data interpretation and process evaluation.

Six potential process routes were identified at an early stage of the project. These were subjected to a preliminary level investigation to determine a preferred option for further study.

Various feeds for the processes were investigated including magnesium and calcium-rich silicate rocks, magnesium-rich brines and carbonates themselves. From this study, magnesium-rich silicate rocks in the form of serpentinite or peridotite were chosen as the most favourable in terms of their reaction chemistry, availability and geographic distribution.

In the event, two methods were chosen for a full financial appraisal.

Method 1 represents the baseline approach and involves the carbonation of solid $Mg(OH)_2$ at elevated temperatures. This has been found to be thermodynamically favourable and has been shown to work at a reasonable rate and yield. The various process steps are summarised as follows:

- *Dissolution Stage:* Acid dissolution, for 15 minutes, at 80°C of fine grained serpentinite feed to produce a slurry.

- *Decantation Stage:* The slurry is pumped to seven 30 m diameter thickeners used for counter-current decantation (CCD) washing. The objective is to remove the silica residue as a slurry from this series of thickeners. The silica slurry is then pumped to the tailings dam for disposal.

- *Dehydration Stage:* The overflow from the final thickener combines with the recirculated magnesium chloride filtrate to form the feed solution to the dehydration stage. This solution is pumped through the multiple effect evaporators where the water driven off in the first effects is used in the precipitators in a subsequent stage of the process, and the water/hydrochloric acid driven off in the final effects is returned to the dissolution stage. The production of the MgOHCl powder is shown to require a further stage of dehydration in the form of a crystalliser.

- *Precipitation Stage:* The MgOHCl powder is conveyed into the precipitators, which produce a magnesium hydroxide precipitate by mixing the powder in water, which comes from the evaporation stage. The slurry produced from these tanks is then pumped to the pressure filters.

- *Pressure Filtration Stage and Drying:* The slurry from the precipitators is filtered under pressure to recover the magnesium chloride solution, which is recirculated to the dehydration stage. The filter cake consists of the magnesium hydroxide and some remaining saturated magnesium chloride solution. A cake of 80% solids has been estimated in order to allow for losses of the magnesium chloride solution at this stage. This loss, together with the loss in the decantation stage, has been taken into account by an increase in the tonnage of rock required in the feed. The filter cake is then conveyed to a rotary dryer, which serves the dual purpose of drying the cake and also breaking up the cake to produce the powder required for the final stage of the process. There will be a small tonnage of hydrochloric acid driven off in the dryer, which will be returned to the dissolution tank

- *Carbonation Stage:* The dry magnesium hydroxide powder is conveyed to the fluidised bed reactors which will operate at 60 bar pressure. There will be several of these units in series, with the removal of CO_2 being performed on a cycle of progressive carbonation of the units in the sequence. An efficiency of 80% has been assumed. Steam at high temperature and under pressure will be generated during this stage that can be utilised in the dehydration stage. The magnesium carbonate and metal oxides are conveyed to the tailings disposal area.

Although the mechanics of the process appear viable, the process suffers from two fundamental flaws which render it commercially unusable:

- The majority of generated energy, from exothermic reactions, condensing water vapour and reforming HCl, is available only as low grade heat. Where this heat can be used, this has been incorporated into the process, but the bulk will go to waste and is unavailable for the major energy hungry processes of dehydration and drying which in practical terms equates to a requirement of more than four times the amount of energy produced by the 500 MW power station for which the process has been designed to accommodate. This translates to a process producing more CO_2 than it sequesters.

- Due to the overall inefficiencies and losses of the process, make-up HCl is required to constantly replenish the reactants for the dissolution stage. For the proposed method, this extra acid represents nearly a third of annual world production.

Taken together, these two critical factors, when combined with the other costs associated with the process route, escalate the sequestration cost to US $233 per tonne of CO_2 (at a 10% discount rate). In addition, total capital costs are shown to be approximately US $640M, whilst total annual operating costs are shown to be approximately US $636M, almost equal to the capital costs.

As an alternative approach, **Method 3b** was also studied in detail. This method was recently suggested by Wendt et al (1998) and involves the direct carbonation of the dissolved silicate in a melt of $MgCl_2$. The process has the principal advantage that it avoids the highly energy intensive dehydration and crystallisation steps which effectively prohibits the commercial development of Method 1. However, although the thermodynamics of the process look favourable, the reaction kinetics are unknown and thus various process parameters have been estimated.

In basic terms, there are three main process stages:

- *Mixing Stage:* Comminuted serpentinite is delivered to the mixing tanks along with the magnesium chloride melt (recycled from downstream processes) and make-up magnesium chloride. A 15 minute residence time has been assumed for this stage. This process will be controlled at 250°C and 2.7 bar, thus, any excess water contained in the melt will be removed by control of the pressure and a bleed system, whilst energy input will be required to drive off the water. The rock will dissolve in the melt and the solution will be pumped to the next stage.

- *Sequestration Stage:* The solution is pumped into autoclaves operating at 30 bar pressure and 300°C, into which the CO_2 is delivered. One hour has been allowed for this reaction to take place. The products of reaction (magnesium carbonate, silica and metal oxides) are removed in the filtration stage that follows.

- *Pressure Filtration Stage:* The slurry is filtered under pressure to recover the magnesium chloride melt, which is recirculated to the dehydration stage at 250°C and 2.7 bar. The filter cake consists of the magnesium carbonate and some remaining magnesium chloride melt. A cake of 80% solids has been estimated in order to allow for losses of the magnesium chloride melt at this stage which must be made up in the mixing tanks. The filter cake is then conveyed to the disposal system.

A total capital cost for Method 3b of US $409M has been estimated, with an annual operating cost of US $195M. The bulk of the operating cost relates to the need to supply additional $MgCl_2$ to the process where a 2.5% loss of melt in the filtration stage is assumed. This requires substantial $MgCl_2$ make-up at a current market cost of US $134M per annum. It should be noted that this represents a significant fraction of current world production.

In summary, Method 3b indicates a sequestration price per tonne CO_2 of US $80.11 at a 10% discount rate and US $78.65 at a 5% discount rate.

The financial model was regenerated assuming the production of $MgCl_2$ make-up on site. With regard to capital cost, installation of the $MgCl_2$ facility increases this to US $422M, whilst operating costs are reduced to US $140M as the process eliminates the need for commercially sourced $MgCl_2$, even though the additional process requires sizeable inputs of HCl, at an annual cost of US $66.7M.

This modified method indicates a sequestration price per tonne CO_2 of US $62.47 at a 10% discount rate and US $60.97 at a 5% discount rate.

A sensitivity analysis was undertaken regarding processing costs. This indicated that very substantial savings in process plant costs (67%), power consumption (67%), fuel consumption

(95%) and make-up chemical costs (95%) would be necessary to reach a target cost of US $20 per tonne of CO_2 sequestered.

In conclusion, although the overall costs and efficiencies of this method are considerably lower than for Method 1, a major problem still exists concerning the large volumes of HCl required as part of the make-up $MgCl_2$ facility, which in its own right may render the process untenable. However, without the $MgCl_2$ facility, the process is equally problematic as an enormous commercial supply of $MgCl_2$ is required for make-up, which is well in excess of current world production.

For either of the main two processes to have a chance at success, the energy hungry dehydration stage in Method 1, and the reliance on huge volumes of make-up chemicals in Method 3b, must be overcome. Further research should thus be targeted at these specific problems.

1.0 INTRODUCTION

1.1 Extent of the Problem

During the last decade or so, considerable scientific efforts have been applied to understand the problems associated with global climate change. One of the major conclusions to come out of this work is the knowledge that CO_2 emissions, primarily from the burning of fossil fuels, have caused a considerable rise in the levels of atmospheric CO_2 concentrations which in the long term may have a significant impact on global weather patterns. At the present time, CO_2 levels in the atmosphere are 30% higher than they were than at the beginning of this century (365 ppm compared to 280 ppm), with more than half of this rise occurring during the last thirty years. Today, the atmospheric CO_2 level is rising at about 1.6 ppm per year whilst worldwide emissions from burning fossil fuels amount to nearly 3 ppm annually. Natural CO_2 sinks account for the difference (Lackner *et al*, 1998).

With world consumption of fossil fuels set to increase steadily into the next century, CO_2 emissions from this source are also likely to increase from their current rates of approximately 22 gigatons per year (Lackner *et al*, 1999). At the present time, the US is responsible for around 25% of this total. Governments have now begun to realise the potential seriousness of the problem and efforts are underway to both limit CO_2 output and also develop new technologies for its disposal. A recent US Department of Energy document (Reichle *et al*, 1999), which is still in draft form, sets a goal to sequester 1 gigaton of carbon (GtC) per year by 2025 and 4 GtC/year by 2050.

To date, a number of less stringent measures, which may have short term benefits, are already being applied to the problem and include general increases in energy efficiencies, switching from coal to oil or natural gas, forestation, and the use of inexpensive renewable energy applications. However, none of the above methods are sufficient to tackle the problem in the medium to long term where specific CO_2 capture and sequestration technologies will need to be developed in conjunction with viable alternative energy sources such as nuclear and large-scale renewable energy projects.

For the capture and sequestration of CO_2, the most cost-effective targets are the fossil fuel power plants which generate large volumes of CO_2 in-situ. Technologies have been developed to allow the separation and capture of CO_2 at the plant, although at the present time, these tend to be expensive and energy intensive. However, assuming that suitable capture methods can be implemented, the prime concern is the ability to develop a low-cost method of permanent CO_2 sequestration which will allow large volumes of gas to be stored safely, and indefinitely.

During the last ten years, the levels of research on the problems of CO_2 capture and sequestration have intensified, although the key factors of finding a suitable method at relatively low cost still apply. From a research perspective, the Japanese have been particularly active in these fields and have instigated major research programmes on CO_2 fixation by microalgae, deep ocean sequestration, and development of permeable membranes for CO_2 capture at source.

As the thrust of this present study is to look at the viability of CO_2 sequestration via the production of stable carbonate minerals, it is probably worth briefly listing other sequestration methods which are, or have, attracted research interest. Increased forestation, although a relatively cheap and efficient method of removing CO_2 direct from the atmosphere, is not included here as it is inapplicable to CO_2 produced at source:

Sequestration into deep aquifers: Statoil of Norway are storing CO_2 into a sandstone aquifer 800 m below the North Sea;

Storage in depleted oil and gas reservoirs: it has been estimated (Herzog *et al*, 1997) that US abandoned oil and gas reservoirs could store up to 2.9 billion tonnes of CO_2, whilst eventually this figure could rise to 100 billion tonnes;

Storage in active oil and gas reservoirs: CO_2 is routinely used for enhanced oil recovery and the process could be modified to optimise storage;

Storage in disused or uneconomic coal seams: CO_2 is used in the recovery of coal bed methane and at the same time, much of the CO_2 that is pumped underground becomes sorbed onto the coal surface and hence remains sequestered;

Storage in salt domes or rock caverns: pre-existing cavities of this type do represent a potential storage site for CO_2, and furthermore, additional salt caverns can be excavated moderately cheaply by solution mining;

Deep ocean sequestration: every year, the oceans take up to one-third of our anthropogenic CO_2 emissions, although the potential storage capacity of the deep oceans is virtually unlimited. However, the environmental impact of such a process has not yet been fully studied. Five methods of ocean storage have been proposed (Herzog *et al*, 1997):

- CO_2 stored as dry ice which is released at surface by ship;
- Liquid CO_2 injected to a depth of around 1000 m from a pipe towed by a moving ship to form a rising droplet plume;
- Liquid CO_2 injected to a depth of around 1000 m from a manifold lying on the ocean bottom to form a rising droplet plume;
- A dense CO_2-seawater mixture created at a depth of between 500 and 1000 m forming a sinking bottom gravity current, and
- Liquid CO_2 introduced to a sea floor depression forming a stable “deep lake” at a depth of about 4000 m.

Reaction with underground brines: Dunsmore (1992) suggested reacting CO_2 with chlorine and sulphate-rich brines pumped from deep evaporitc basins, to produce stable mineral carbonate;

CO_2 capture by microalgae grown in proximity to power plants: fast growing microalgae represent a potential means of capturing CO_2 at source, although the large pond storage area required is thought to be detrimental factor.

Many of the above methods have merit for the long term sequestration of CO_2, but in all cases, considerable additional work is required to define the suitability, economic viability and environmental impact of such methods.

1.2 An Alternative Approach

The concept of sequestering CO_2 within stable mineral carbonates is relatively new, although the chemistry behind the various reactions is well known. The only common oxides that readily form stable mineral carbonates are calcium and magnesium, although in nature, pure CaO and MgO are rare. However, many common minerals can be considered as combinations of these oxides with others forming a silicate matrix.

It has long been observed that through geologic time, naturally occurring silicate rocks rich in magnesium and calcium, which themselves are generally stable, breakdown through weathering to a variety of products dependent on the chemistry of the original parent rock types and the mode of weathering prevailing (Kojima *et al*, 1997). Early geologists observed that two common products from such processes are magnesite ($MgCO_3$) and calcite ($CaCO_3$).

Of particular interest to the concept of CO_2 sequestration is that the weathering process is in effect sequestering CO_2 from the atmosphere to produce a stable carbonate product. Clearly, this process takes place over millennia, but the chemistry of the reactions is relatively simple and can be demonstrated to work at the laboratory scale and probably as part of an industrial process.

The starting points for such reactions are the magnesium and calcium which occur as silicates in a variety of rocks and make up 2.0 and 2.1 mol% respectively of the Earth's crust, although magnesium silicates contain more reactive material per tonne due to the lower molecular weight of magnesium. Also, pure deposits of magnesium silicate rocks are more common in nature than their calcium-rich counterparts (Goff *et al*, 1998). In addition, two relatively pure magnesium silicate minerals, forsterite and serpentine, occur in discrete deposits, or as minerals within peridotites and serpentinites respectively, which in turn are often part of a suite of rocks known as ultramafics.

From a logistical standpoint, the distribution and size of these various rock units around the world is more than adequate to satisfy the requirements of power generation CO_2 sequestration. Major ultramafic formations can be found in USA, Europe, Japan, India, Russia and China. More importantly, there are no major emitter countries without such a source.

Lackner *et al*, (1998) have highlighted the intrinsic advantages of mineral carbonation over other forms of CO_2 disposal:

- The disposal of the mineral carbonate is safe and the waste products are stable, environmentally benign and non-hazardous with no possibility of accidental CO_2 release;

- Mining and waste disposal occur at the same site, thus minimising the environmental impact;
- Long-term monitoring of the disposal site is not required, and
- The various rock types suitable for the sequestering process are plentiful in nature.

However, it should be emphasised that large waste tips and tailings dams have caused environmental and safety problems in the past, and care should be exercised with site selection, construction and management. In addition, it is likely that the waste product will have a volume approximately 50% greater than the raw material.

Apart from utilisation of magnesium or calcium-bearing silicates to provide the feedstock for mineral carbonation, Dunsmore (1992) has suggested that magnesium chloride-rich brines, which occur in certain parts of the world, may provide an aqueous source of magnesium ions which could be suitable for the sequestering process.

In addition, a method first proposed in 1866 by Weldon and since modified and adapted by Robertson (1995), has also been considered. The Weldon process was originally designed as a method for the production of sodium bicarbonate, although it was never attempted on an industrial scale, possibly as a consequence of the corrosive nature of the reaction and the pressure of CO_2 required to drive the reaction. However, although the method produces sodium bicarbonate, it can also be used to sequester CO_2, even though ironically, the starting products are a carbonate (dolomite) and sodium chloride.

Thus, the various approaches discussed above for CO_2 sequestration all utilise a naturally occurring feedstock and produce a mineral carbonate product with a variety of bi-products. Thus, this study will evaluate the various processes on a number of key issues:

- Nature, quantities and distribution of source material;
- Efficiency of the process reactions;
- Confidence in the scale, complexity and demand needs of the process;
- Overall cost of the process, and
- Public acceptance of the environmental, safety and social issues.

Although the logistics and chemistry of the various process options can be considered in some detail with a fair degree of accuracy, the decision as to whether a method can be cost effective can only be based on 1999 parameters. Consequently, measures, such as the application of CO_2 tax (Denmark, Finland, Norway, Sweden and The Netherlands have already introduced taxes on industrial emissions), or other punitive legislation, may drastically change the economics of any one process.

1.3 Report Structure

The report presents the overall potential of CO_2 sequestration as stable mineral carbonates. The study considers a number of process options, using currently available data, from which a baseline approach and modified version were evaluated.

The extent of the problem of CO_2 sequestration and the possible alleviation methods are discussed in Section 1, whilst the type and availability of potential source rocks are considered in Section 2.

The mining and preparation of the basic raw materials for the sequestration process are discussed in Section 3, followed in Section 4 by a detailed critique of the different chemical reactions relevant to the various process options.

Section 5 provides a synthesis of each of the six chosen process options and attempts to make comparisons between options to allow the selection of a preferred method for more detailed study. This is followed by Section 6 which presents a broad discussion on the environmental and social implications of each of the process options.

Section 7 forms the core of the report by considering a costed feasibility for the preferred process option as defined in Section 5, whilst Section 8 provides a more detailed study of a kinetically unproven method which may represent a viable process option in the future.

The report concludes with Section 9 which provides a summary of the salient points of the work, and importantly, gives recommendations as to the direction of future research.

2.0 POTENTIAL SOURCE ROCKS

2.1 Type

It has been shown that common calcium and magnesium silicates alter to their respective carbonates by mild exothermic reaction and under thermodynamically favourable conditions (Lackner et al, 1995). As already mentioned, this process occurs naturally over geologic time.

Calcium and magnesium oxide-bearing silicate rocks are prevalent throughout the world. Calcium oxide concentrations, and thus the reactive part of the silicate, are of the order of between 9 and 13%, whilst magnesium oxides may reach up to 50% or more, although it should be noted that these oxides are locked within the silicate matrix. This clearly indicates that from a mineral processing perspective at least, considerably smaller amounts of magnesium-bearing rock would be required for any sequestering reactions in comparison to their calcium equivalents (Lackner et al, 1997).

A selection of abundant rock types which are rich in magnesium and calcium oxides has been compiled by Lackner et al, 1995. The results of this study are illustrated in Table 2.1 below:

Table 2.1: Abundant Rock Types Rich In Magnesium And Calcium

Rock Type		MgO wt%	CaO wt%	R_C	R_{CO2}
Peridotites:	Dunites	49.5	0.3	6.8	1.8
	Harzburgite	45.4	0.7	7.3	2.0
	Lherzolite	28.1	7.3	10.1	2.7
Serpentinite		~40.0	~0.0	~8.4	~2.3
Gabbro		~10.0	~13.0	~17.0	~4.7
Basalt:	Tholeiite	6.2	9.4	26.0	7.1

Where: R_C is the mass ratio of rock needed for CO_2 fixation to carbon burned.
R_{CO2} is the corresponding mass ratio of rock to CO_2.

It can be seen from the data presented above that peridotites and serpentinites would appear to have the most potential for sequestering CO_2 as their mass ratios of rock to CO_2 are relatively low, at values between 1.8 and 2.7. However, because of their lower densities and high water contents, serpentinites contain substantially less Mg than peridotites.

The scope of work for this project calls for the sequestration of approximately 3 Mt of CO_2 per year. Given the above information, rock tonnages required of either peridotite or serpentinite would be in the order of 5.5 to 8 Mt per year respectively, whilst for a typical basalt, that figure is likely to be in excess of 20 Mt, assuming the sequestration process is taken to completion.

Another suggested source material is magnesium-rich brine, which although already in aqueous form, has the disadvantage that magnesium concentrations are generally low (10 –

15% $MgCl_2$ on average), thus requiring large volumes of solution (approximately 1.4 million litres per hour) to meet the CO_2 storage target.

Alternatively, using dolomite ($CaMg(CO_3)_2$) as a potential feedstock again requires much higher tonnages (approximately 15 Mt per year) when compared to a magnesium silicate route, as the weight percentage of magnesium in dolomite is much lower than the corresponding silicates.

A more detailed description of the mineralogy and chemistry of the various source materials is presented below.

2.1.1 Serpentinites

Serpentinites are rocks composed predominantly of the serpentine minerals lizardite, chrysotile, and antigorite, with accessory magnetite, brucite, and Mg and Ca-Al silicates (O'Hanley, 1996).

Serpentinites are secondary in nature and form by the chemical alteration of peridotite, pyroxene, gabbro, marble and siliceous dolomite. They are generally stable below 550^{o}C, with lizardite and chrysotile stable below 300^{o}C. The alteration process may be pervasive throughout the protolith (original rock), or along fractures and joints which yields vein-like serpentinite.

The three serpentine minerals are isochemical with very similar sheet-like structures. When subjected to stress, chrysotile sheets roll into the elongate fibres known as asbestos. Lizardite and chrysotile are the most common serpentine minerals and form at lower temperatures than antigorite (<250^{o}C). The hydration of forsterite to form serpentine (and brucite ($Mg(OH)_2$)) is accompanied by a volume increase of as much as 53%. Thus, pure serpentinites are low density rocks (2.6 g/cm^3) as compared to the original peridotites (3.3 g/cm^3), and in addition, may contain as much as 14 wt% water.

With relevance to the concept of sequestering CO_2 as stable carbonate minerals, it is well known that the carbonate minerals magnesite, calcite and dolomite replace serpentinite by a process known as carbonitisation. This process takes place at low temperature, resulting in a mineral assemblage of either talc + carbonate or quartz + carbonate, with or without relict serpentine.

As a reflection of the CO_2 sequestering potential of serpentinites and their associated rocks, Table 2.2 below provides the MgO% for a number of samples (after Goff et al, 1997):

Table 2.2: MgO% of selected serpentinites and associated rocks

Sample	1	2	3	4	5	6
Locality	Del Puerto, California	Del Puerto, California	San Mateo, California	Wilbur Springs, California	Baltimore Complex, Maryland	Belvidere Mountain, Vermont
Type	Altered Peridotite	Massive Serpentinite	Sheared Serpentinite	Massive Serpentinite	Serpentinite	Serpentinite
MgO%	42.5	34.7	33.1	36.2	35.1	38.0

2.1.2 Peridotites

Peridotite is a generic term to define a group of rocks with quite similar, but subtly different mineral chemistry. Peridotites consist of >90% olivine, pyroxene and hornblende, with olivine being predominant. Other minerals present include plagioclase feldspar, chromite and garnet.

All peridotites are rich in Mg and have high Mg:Fe ratios (these ratios are similar to those found in meteorites), and they usually contain significant concentrations of Ni and Cr, sometimes up to ore-level concentrations. Characteristically, peridotites are also commonly altered to serpentinites, and thus the two rock types are often found together in geology.

The various names given to the peridotite family are dependent on the subordinate mineral chemistry of each member (Coleman, 1977). Most alpine peridotites (see below) consist primarily of Mg-rich olivine (forsterite, $(Mg,Fe)_2SiO_4$), with lesser amounts of Mg-rich orthopyroxene (enstatite, $(Mg,Fe)SiO_3$), clinopyroxene, and chromite (chrome spinel, $FeCr_2O_4$). The clinopyroxene, usually Cr-rich diopside, contains some Ca, Al, Ti, and Na. Typical alpine peridotites contain ≥10% orthopyroxene and are called harzburgites, whilst if the composition changes to ≥10% clinopyroxene, the rock is termed a lherzolite. Peridotites with ≥90% olivine are called dunites.

With regard to sequestration potential, the MgO content of a variety of dunites, harzburgites and lherzolites is illustrated in Table 2.3 below (after Coleman, 1977).

End members commonly grade into one another, particularly in layered intrusions which are a typical host for peridotites, although their presence in ophiolite complexes (see below) is extremely important to their geographic distribution. In general terms, peridotites represent fragments of deep mantle material (Hess, 1989) and are found in a variety of geologic settings around the world.

Table 2.3: MgO content of a variety of ophiolitic peridotites

Rock Type	**MgO%**										
Dunites	50.6[1]	49.8[2]	47.7[3]	50.9[4]	50.3[5]	48.1[6]	49.3[7]	49.1[8]	49.7[9]		
Harzburgites	45.9[1]	45.3[10]	44.4[3]	45.7[4]	45.2[5]	39.6[6]	44.7[11]	48.1[12]	45.7[8]	45.2[13]	48.4[9]
Lherzolites	38.9[14]	39.6[15]	11.3[15]	9.9[14]	40.9[16]	41.3[17]					

[1]Burro Mountain, California; [2]Twin Sisters, Washington; [3]Red Mountain, California; [4]Vourinos, Greece; [5]New Caledonia; [6]Horoman, Japan; [7]Dun Mountain, New Zealand; [8]Trrodos, Cyprus; [9]Papua New Guinea; [10]Cazadero, California; [11]Red Hills, New Zealand; [12]Bay of islands, Canada; [13]Semail, Oman; [14]Ronda, Spain; [15]Beni Bouchera, Morocco; [16]Lanzo, Italy; [17]Estimated Upper Mantle

2.1.3 Basalts

Basalts are basic igneous rocks which in general are black, fine grained and can vary from rather dense to relatively light, depending on the amount of vesicles present. Mineralogically, they comprise phenocrysts of olivine, pyroxene or plagioclase enclosed in a groundmass of very fine plagioclase, pyroxene, olivine and magnetite, with a wide range of accessory minerals.

Basalts have formed in a variety of geologic environments which have imparted subtle differences in their chemical compositions. Hall (1987) suggests that the main compositional varieties are:

- *Ocean floor basalts:* these are tholeiitic in composition and are formed at divergent plate margins and as such are often termed mid-ocean ridge basalts (MORB). They are very low in K, Ba, P, Sr, U, Th and Zr, and low in Fe_2O_3/FeO and K_2O/Na_2O.
- *Volcanic arc basalts:* which are formed at convergent plate margins, either at island arcs or continental margins, and range from tholeiitic to alkalic in composition. Generally, these rocks are high in K_2O and low in MgO compared with ocean floor basalts.
- *Within-plate basalts:* these can occur in oceanic or continental settings, and often have varied composition, from tholeiitic to strongly alkalic.

Trace element geochemistry also varies between basalts and can be useful in identifying the original paragenesis of the magma.

From a sequestration perspective, it is the CaO content of the basalt which is important. Cox et al (1979) have tabulated average values based on 26,373 analyses for a large number of different rock types, including basalt (Table 2.4):

Table 2.4: Average basalt composition in % (After Cox et al, 1979)

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	**CaO**	Na_2O	K_2O	P_2O_5
49.20	1.84	15.74	3.79	7.13	0.20	6.73	**9.47**	2.91	1.10	0.35

It can be seen from the data above that the average CaO content is up to five times lower than a typical dunite, thus requiring far more calcium than magnesium silicate feed for the CO_2 sequestration process.

2.1.4 Magnesium-rich Brines

Brines rich in magnesium are relatively rare in nature and if present, are almost always associated with other chloride solutions such as calcium and sodium (often with minor strontium, lithium, bromine and boron). Other brines commonly also contain magnesium sulphate and potassium chloride.

Geologically, there appears to be three principal environments from which magnesium-rich brines may be extracted directly or as bi-products:

- Aquifers, where the brine is in relatively concentrated form;
- As constituents within surface saline lakes (Great Salt Lake, Utah, contains up to 14% $MgCl_2$), and
- As a bi-product from solution mining of potassium/magnesium-bearing salts.

As an example, Harben and Kužvart (1996) cite the composition of an aquifer brine within the Devonian Filer Sandstone Formation in Michigan, USA as 9.4% $MgCl_2$, 17.6% $CaCl_2$, and 3.5% NaCl, as well as less than 1% each of $SrCl_2$, KCl, LiCl, Br and B.

By far the largest potential for magnesium-rich brines are as bi-products from solution mining of deep evaporite deposits (usually >1000 m). An example of this is the brine generated from the Veendam sequence in the Groningen province, Netherlands. Here, solution mining extracts the carnallite ($KCl.MgCl_2.6H_2O$), bischofite ($MgCl_2.6H_2O$) and kieserite ($MgSO_4.6H_2O$), from the extensive Permian Zechstein sequence of northern Europe. The raw brine produced contains approximately 20% $MgCl_2$, 1–2% $MgSO_4$, 4–5% KCl and 2% NaCl.

In conclusion, although rare in nature as relatively pure products, magnesium-rich brines can be extracted from other soluble salts such as carnallite and bischofite. However, these evaporite deposits carry many impurities and vary in composition often over very short lateral distances, thus making recovery of a standard product difficult.

2.1.5 Dolomite

Dolomite is a double carbonate of calcium and magnesium ($CaMg(CO_3)_2$) which has a theoretical content of 45.7% $MgCO_3$ 54.3% $CaCO_3$. The MgO equivalent content is 22% by weight. The term dolomite is also applied to dolomite rock, which is a limestone that has been partly transformed to the mineral dolomite. A true dolomitic rock contains over 39% $MgCO_3$ (Roskill, 1990).

More commonly occurring is dolomitic limestone which is deemed to have an $MgCO_3$ content in excess of 20%, whilst those rocks with a range of between 5–15% are termed magnesian limestone.

Dolomite rock typically occurs in two forms (Pettijohn, 1975):

- An early, primary fine-grained crystalline dolomicrite which occurs characteristically in thin, commonly laminated beds, and
- Later, epigenetic replacement of limestone which appears generally as coarsely crystalline or sacharoidal dolomite.

The latter form of dolomite is by far the most common in nature, although due to the manner of the replacement, the $MgCO_3$ content of these rocks can be very variable. Pettijohn (1975) has published some typical data (Table 2.5):

Table 2.5: Chemical composition (%) of dolomites (After Pettijohn, 1975)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
A[1]							21.9	30.4			
B[2]	2.55	0.02	0.23	0.02	0.18	0.04	7.07	45.65	0.01	0.03	0.04
C[3]	7.96	0.12	1.97	0.14	0.56	0.07	19.46	26.72	0.42	0.12	0.91
D[4]	3.24		0.17	0.17	0.06		20.84	29.58			
E[5]	24.92	0.18	1.82	0.66	0.40	0.11	14.70	22.32	0.03	0.04	0.01
F[6]	0.73		0.20		1.03		20.48	30.97			0.05

[1] Theoretical composition of pure dolomite; [2] Dolomite Limestone, Ohio; [3] Niagaran Dolomite, Ohio; [4] Knox Dolomite, Alabama; [5] Cherty Dolomite, Ohio; [6] Randville Dolomite, Michigan

Commercial deposits, for magnesium production, have to be large (usually >10 Mt), and to be of high purity, strength and density. This is often difficult to achieve as older dolomites tend to have lower purity but higher strength and density, whilst younger dolomites show the opposite.

In conclusion, as is evident from the above data, the magnesium content of dolomite is highly variable, thus requiring careful selection for a suitable sequestering medium.

2.2 Distribution

The close association of serpentinites and peridotites allows their geographic distribution to be described together, grouping them under the classification of ultramafic rocks which can form in a variety of geologic settings which are too numerous to detail here. Coleman (1977) provides a good classification for such rock types, whilst Gass (1982) presents a refined model for their emplacement. However, large, unaltered peridotites are less common in nature than serpentinites because of their high reactivity in the geologic environment.

For the purposes of this study however, two such classes of ultramafic rocks will be discussed, notably ophiolites and layered intrusions.

2.2.1 Ophiolites

The typical setting for such rocks is as fragments of mantle material which have been caught up in crustal orogenesis. Such bodies are typified by large peridotite masses located in major mountain fold belts, often described as alpine peridotites (Hess, 1989). If portions of oceanic crust are included within the peridotite assemblage, these rocks are then often termed ophiolites.

Ophiolites represent slabs of oceanic crust which have been thrust upwards and eroded along plate boundaries and subduction zones, with the basal peridotites representing detached slices of upper mantle caught up in the orogenic process.

Due to their association with plate boundaries, ophiolites are often located in discrete belts, commonly, but not exclusively along continental margins. As a consequence, serpentinites and peridotites can be found in many parts of the world (Figure 2.1).

Well documented ophiolite belts include:

- Troodos Mountains in Cyprus;
- Tethyan Ophiolites of the European Alps (type region);
- Simail Ophiolite in Oman;
- Bay of Islands Ophiolite, Newfoundland;
- Eastern Papua Ophiolite, Papua New Guinea;
- Caribbean belt;
- Chaucas Ophiolite, Guatemala;
- Cordilleran belt, west coast USA;
- Appalachian belt, USA;
- Zagros Mountains, Iran;
- Lizard Complex, UK, and
- Various Japanese ophiolite units.

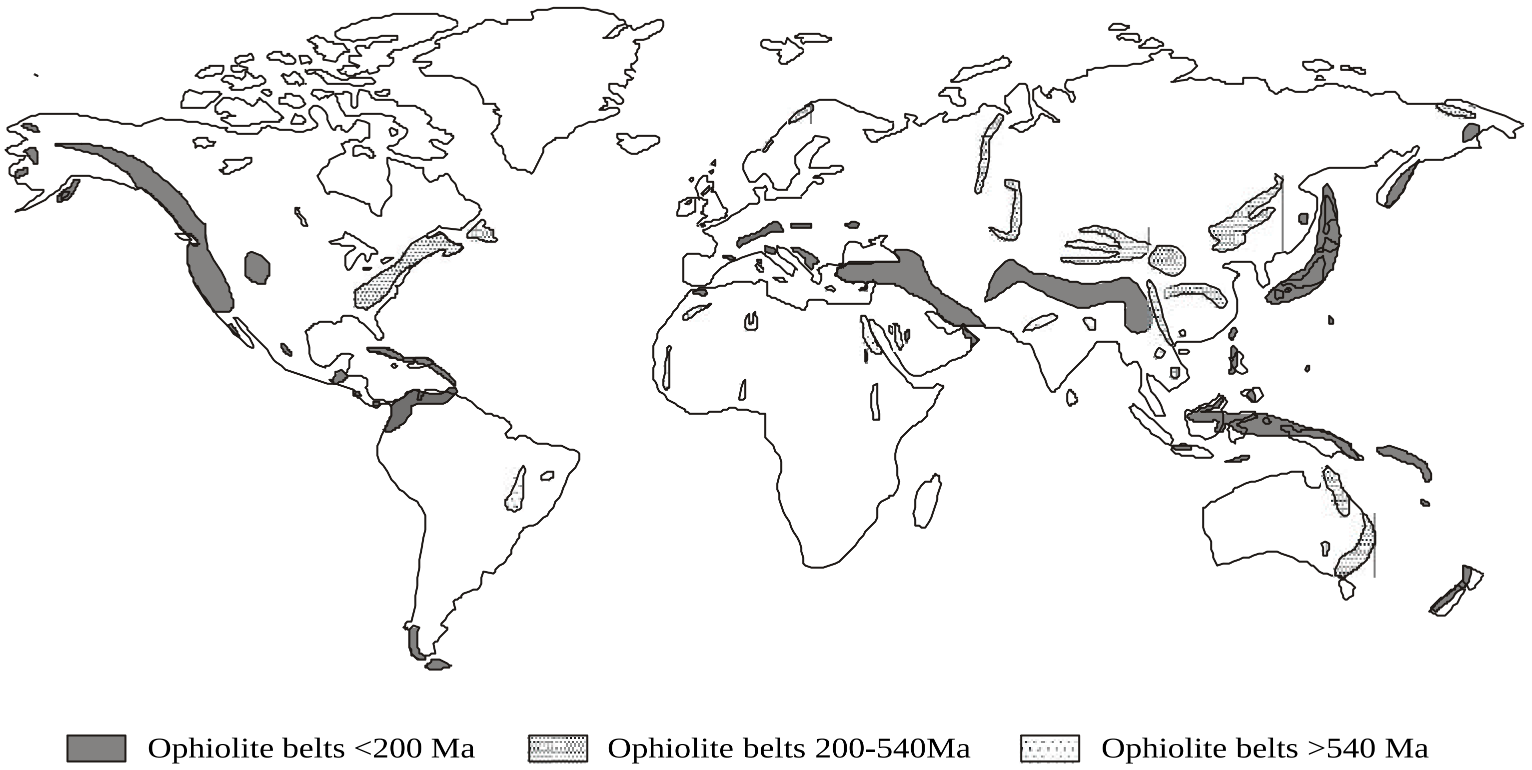
It is noticeable from the above list that the African subcontinent has very few ophiolite complexes, although small ancient ophiolitic bodies containing peridotites and serpentinites do occur in several parts of the continent.

2.2.2 Layered Intrusions

A second class of ultramafic rock that has importance for this study is the large layered intrusion, of which the Bushveld Complex in South Africa is the biggest. These intrusions are sporadically distributed around the world, and are often, although not always, associated with ancient Archean age rocks.

It is thought that these large magma bodies of similar composition to the mantle, were intruded into shallow levels of the crust. Due to their large size, slow cooling allowed fractional crystallisation to take place which tended to cause early crystallising Mg-rich

Figure 2.1: Location and age (millions of years - Ma) of the main ophiolite belts of the world



silicates to settle by gravity to the base of the intrusion. Thus, some of the larger intrusions contain peridotite layers several hundreds of metres thick.

Major examples of these bodies include:

- Bushveld Complex, South Africa;
- Stillwater, Montana, USA;
- Sudbury, Canada;
- Skaergaard, Greenland, and
- Rhum Complex, Scotland.

It is interesting to note that several of these large layered bodies are currently being exploited for their mineral resources, for example, Bushveld for chromite and platinum, Stillwater for platinum group metals and Sudbury for nickel and copper.

It is beyond the scope of this study to describe these bodies in detail, although Cawthorn (1996) provides an excellent text on the geology, mineralogy, chemistry and tectonic setting of these layered intrusions.

2.2.3 Basalts

Due to their genetic diversity (2.1.3), basalts are found commonly throughout the world, and thus would make them an ideal feedstock with regard to plentiful and well distributed supplies. As an example, Lackner et al (1996) briefly mention the Columbia/Snake River flood basalt in North America which has an average thickness of about 1 km and an estimated volume of some 200,000 km^3. This basaltic body alone could absorb all the CO_2 generated from the estimated world coal reserves 2.5 times over.

However, the scale of the Columbia basalts pales to insignificance when compared to the magnitude of the Deccan traps in India which represent the world’s largest outpouring of basaltic magma.

Thus, from a distribution perspective, basalts are ideally suited as a feedstock for the sequestration process.

2.2.4 Brines

The geographic distribution of brines is somewhat restricted in that although they are generally associated with evaporite deposits, they require the correct chemistry of the mineral constituents, i.e., carnallite and bischofite must be present in large quantities, and in reality, many evaporite sequences are dominated by sodium and potassium chlorides.

At the current time, magnesium-rich brines are extracted from a number of locations around the world:

- Brine within the Filer Sandstone, Michigan, USA;
- Great Salt Lake, Utah, USA (bi-product from potash production);
- Laguna del Rey, Mexico;
- Groningen, Netherlands (from solution mining of evaporite minerals), and
- Dead Sea, Israel.

However, as can be seen from above, the current level of brine production is relatively small, although some of the large evaporite basins of the world do offer the opportunity to develop brine recovery from solution mining of major potash deposits. It is worth considering that one quarter of the world's continental landmass is underlain by evaporite rocks, of which about 60% contain chlorides.

Typical examples of large evaporite basins that contain suitable potash salts include (Melvin, 1991):

- Elk Point Basin, Saskatchewan, Canada: this basin, which is approximately 325 km wide and 1,300 km long, is the world's largest producer of potash by both underground and solution mining methods;
- Castile Formation, Texas, New Mexico, USA: this basin underlies an area approximately 350 km in diameter and the deposits are worked for gypsum, anhydrite, potash and salt;
- New York Salina;
- Permian Zechstein basin of northern Europe, and
- West African basin: this area is currently generating interest for magnesium production from solution mining of the extensive potash and magnesium salt beds.

Although evaporites are relatively common, delineating those with sufficiently high magnesium contents, the correct depth profile, suitable location, and minimal trace element contaminants, presents difficulties in using them as a feedstock for the sequestration process.

The exception to this may be the Saskatchewan deposits as they seem to offer opportunities for Ca-Mg brine extraction and are well placed to mitigate CO_2 production from local open cast coal. However, further studies would be required to test this scenario.

2.2.5 Dolomite

Dolomite occurs in rocks of all ages, but tends to be more common in Palaeozoic rocks and older (Pettijohn, 1975). It is usually associated with limestone with which it is interbedded on a range of scales from a few centimetres up to hundreds of metres.

Large deposits of dolomitic limestone are distributed widely around the world, but no attempt has been made to estimate world deposits on a systematic basis primarily because reserves are many times current production needs which have been estimated at >100 Mt.

As examples of important world sources of dolomite, in the USA, there are four major dolomite areas. These are in the Appalachian Valley and Ridge, extending from Vermont to Alabama, Western Ohio and Eastern Indiana, a U-shaped belt stretching from Minnesota to the northern shores of Lake Michigan and Lake Huron, and an area of Southern Missouri and Northern Arkansas.

In the UK, dolomite occurs in the Magnesian Limestone series which outcrops in a narrow belt from Nottingham to the coast near Hartlepool, in the Carboniferous Limestone in Derbyshire and also in South Wales, and in Scotland in the Appin Limestone of Argyll and the Durness Limestone in the north. There are also significant dolomite occurrences in Ireland.

Other countries which produce substantial quantities of dolomite include Canada, Belgium, Austria, Poland, Germany, Spain, Sweden, Finland, Luxembourg, Netherlands, Romania, CIS, Venezuela, Brazil, South Africa, Zimbabwe, India, Japan and South Korea.

In conclusion, the geographic distribution of dolomite is more than adequate to supply the needs of a potential CO_2 sequestering medium.

2.3 Economic Significance

If the chemistry and logistics of utilising a particular feedstock are put to one side for the time being, then one of the major factors which will govern whether a potential feedstock is suitable for CO_2 sequestration will be the availability of the material in relation to the proximity of existing coal fired power plants. Clearly, this will be of primary economic concern for two principal reasons:

All the potential feedstocks described above (with the exception of brines) are high bulk, low value commodities which will economically preclude long transport hauls to the sequestering plant, i.e., the plant needs to be at the site of the feedstock, and CO_2 will have to be transported to the sequestration plant (probably by pipeline), and thus it is prudent to also minimise this transportation distance where possible.

Consequently, an ideal scenario will have plentiful feedstock available for sequestration adjacent to a major coal fired power plant, and in some parts of the world, this scenario can be achieved.

From a distribution and commonality standpoint, basalt and dolomite are by far the most geographically widespread of the various potential feedstocks described above. With regard to their distribution in terms of coal fired power plants, dolomite in particular is well placed, as being a sedimentary rock, its occurrence is often associated with other carbonate rocks such as limestones which are in turn are often adjacent to, or interbedded with, coal measures, which historically have tended to favour power station location. A good example of this is eastern USA where plentiful supplies of dolomite exist in close proximity to modern coal fired power plants.

Similarly, although basalts have no geologic link with coal deposits, their broad crustal distribution indicates that a supply of the material will usually be available in relatively close proximity to existing coal fired power plants.

Although far less common than either dolomite or basalt, as outlined above, the availability of serpentinite and peridotite rocks worldwide is quite high, and more importantly, many sites are relatively close to industrial centres, and in particular, coal fired power plants. Good examples of this are the Cordilleran and Appalachian belts of USA, Tethyan ophiolites of the Alps (Europe), and the numerous ophiolite bodies of Japan and Indonesia.

Although the economics and viability of transporting captured CO_2 to the sequestering plant are beyond the scope of this study, it is evident that the distance between power plant and sequestering site is a critical factor, as pipeline costs (the likely medium for CO_2 transport) will impinge on the overall viability of the process.

Goff *et al* (1997) have taken this reasoning one step further by considering a specific ultramafic province with regard to its potential as a site for CO_2 sequestration. They have used several Californian ultramafic bodies to illustrate the magnitude and potential of such bodies, and in turn, have compared these with the Stillwater layered deposit in Montana. Table 2.6 presents the summary results from this study.

Table 2.6: Morphology and Sequestering Potential of a Number of Peridotite/Serpentinite Bodies (after Goff, 1997)

	Peridotite/Serpentinite Body							
	Del Puerto	Stillwater	Wilbur Springs	San Mateo	Vulcan Peak	Twin Sisters	Belvidere Mountain	Baltimore Complex
Mineralogy								
Dunite	4	4			4	4	4	
(alteration)	4	4			4		4	
Harzburgite	4	4			4	4		
(alteration)	4	4			4			
Serpentinite	4	4	4	4	4	4	4	4
(alteration)	4	4	4	4	4		4	4
Area (km^2)	40	26	200	4	16	91	2.3	100
Depth (km)	0.3	0.5	>0.2	0.25	0.5	0.6	<1	0.3
Wt% Mg	23	17	21	20	27	29	26	21
RCO_2	2.40	3.25	2.63	2.76	2.05	1.91	2.13	2.61
CO_2 (10^9 t)	14.0	12.4	40.3	0.9	12.5	94.1	2.7	30.8

Where RCO_2 is the calculated mass ratio of rock processed for each unit of CO_2

From the data presented above, it is evident that a number of ultramafic bodies in the US could sequester large volumes of CO_2.

For the purposes of an illustration, if completely mined, the Del Puerto site would yield over 7.7 Gt of Mg which could sequester approximately 14 Gt of CO_2. Although the tonnages seem huge, put into context, the US produces approximately 5 Gt of CO_2 per year, whilst world production is estimated at 19 Gt.

An additional important point is that should this ultramafic body be mined out, large tonnages of subsidiary metals would also be produced including approximately 2 Gt of Fe, about 80 Mt of Cr, 80 Mt of Ni and 30 Mt of Mn. These production levels would have a serious impact on world metal prices and would affect the economics of many existing metal producers.

As a European example, the Lizard Complex in Cornwall, UK, is dominated by peridotite, amphibolite and gabbro with significant amounts of granitic material and metasediments. The complex has been interpreted as slices of an obducted ophiolite (Selwood et al, 1998). The peridotite, which is a coarse-grained spinel-lherzolite, is variably serpentinised and contains pockets of dunite, areas of talc alteration and secondary magnesite. Purely from a sequestering perspective, the peridotites, which are of variable thickness, occupy an area of approximately 50 km^2 and can therefore be considered to be a significant resource.

2.4 Conclusions

From the above examples, it is clear that the potential for ultramafic bodies to sequester very large tonnages of CO_2 is considerable, and that their geographic location is generally favourable for supplying the needs of the world's major urban areas.

Of even wider geographic spread and density are dolomite and basalt which can be commonly found in plentiful supply in virtually any region of the world. Dolomite in particular is often found in association with coal basins which historically have been the site for fossil-fuel power plants.

In contrast, the worldwide distribution of magnesium-rich brine deposits is very limited, although as discussed, magnesium-bearing evaporite deposits are quite common. From an economic perspective, it seems unlikely that the magnesium-rich brines could have a major impact as a potential feedstock for sequestration, although on a local, site specific basis, they may have some application.

However, if all other factors are excluded, solution mining of magnesium-bearing evaporite deposits could satisfy the supply of brine at a global level, although the logistics of this process are believed to be difficult.

As a footnote to the potential mineral carbonate sequestration routes outlined above, it is interesting that some modern-day highly alkaline lakes, often adjacent to areas of ultramafic rocks, are strongly enriched in magnesium, and that within these water bodies, hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$) is being deposited as stromatolites (algal mats), and as re-worked hydromagnesite sediment around the lake shores (Braithwaite and Zedef, 1996). Salda Lake in Turkey is referenced, and it has been proven that deposition of the hydromagnesite is independent of both lake level and concentration of lake waters, indicating that the presence of algae has acted as the stimulus for the process, with the CO_2 being supplied directly from the atmosphere.

Similar studies on sedimentary lacustrine magnesite deposits in Yugoslavia (Morteani *et al*, 1982) also show that historically magnesite has formed as a precipitate within a lake environment, interbedded with marls and sandstones. Whether algae had a part to play in this deposition process has not been investigated.

Recent work by Russell *et al* (1998) has added to the discussion by suggesting that the “White Rock” seen on Mars which measures some 18 x 15 km x 180 to 540 m high, is a lens of magnesium carbonate which has formed from precipitation of ground waters which have seeped into an ancient evaporating crater lake. Furthermore, Russell suggests that the trigger for precipitation may have been the development of stomatolites which are seen as analogous to the Salda Lake example described above. As a side issue, Russell suggests that this clearly represents evidence of ancient life on Mars.

These various examples of microalgae acting as catalysts for the precipitation of magnesium carbonate may provide a further area of research not previously considered by other workers for the storage of CO_2 as a stable mineral carbonate.

3.0 MINERAL EXTRACTION AND PRIMARY PROCESSING

3.1 Introduction

Since the outset of studies into the concept of CO_2 sequestration within a stable mineral carbonate, it has been known that considerable feedstock would be required to satisfy the demand of a medium sized coal fired power station. However, should a hard rock feed be the preferred approach, the anticipated tonnages are well within the scope of modern mining operations.

In addition, the construction and operation of large scale open pit mining operations and their associated costs are well documented in Western terms (Mining Cost Service, 1998; Pinock, Allen & Holt, 1989; Noakes and Lanz, 1993). Variations will occur according to a number of differing parameters, but a generic case is assumed for this study.

Open pit mining worldwide has production scenarios ranging from several hundred tonnes per day up to the larger operations, such as copper mines, producing 1 Mt per day for an annual total exceeding 300 Mt. Table 3.1 provides production data for a number of mining operations throughout the world.

Table 3.1: Examples of Open Pit Mines With Annual Production

Mine	Country	Total Mined (Mt pa)
Palabora	South Africa	32
Chuquicamata	Chile	112
Grasberg	Indonesia	345
Escondida	Chile	256
Bingham Canyon	USA	108
Collahuasi	Chile	130
OK Tedi	Papua New Guinea	57

Mining large tonnages at remote locations around the world is not considered to be problematic by today's engineering standards. Economies of scale come very much to the fore in assessing the relative costs of such operations as does the geographic location.

Similarly, large scale pumping operations such as those required for the brine extraction method are known from the water and oil industries, but current brine pumping operations do not remotely approach the expected levels of production.

3.2 Mining

The mines listed in Table 3.1 above are copper or copper/gold producers where the ore extracted only represents a proportion of the total tonnage moved. For example, Escondida extracts approximately 5.5 t of waste rock for every tonne of payable material, whilst Palabora extracts 0.2 t of waste for every tonne of ore. These ratios of ore to waste are known as stripping ratios and are an important factor in the economics of any mining operation.

In both examples above, mining and moving the ore and waste material requires the same equipment and consumes the same general costs, although the costs are often reported relative to the quantity of ore treated in the process plant. The main factors which dictate these stripping ratios are grade of material mined and the geometry of the geological resource.

In the scenario envisaged for this study, an open pit mining operation providing some 8 - 13 Mt per annum of product is assumed. In mining terms this can be considered a medium sized operation with associated costs somewhat higher than those achieved for the larger operations mentioned above. However, it is assumed that the occurrence of the ultramafic rocks are such that no allowance has to be made for any waste stripping other than minimal surface detritus. The rocks are assumed to have a favourable geometry in relation to their country rock hosts and accordingly all rock drilled and blasted is moved as CO_2 sequestration product to a suitable process facility.

Thus, the open pit operation would extract the rock by conventional drill and blast techniques, producing a benched pit whose shape would be dependent on the geometry of the orebody. The ore would be loaded into trucks by shovel before being transported to the comminution plant for primary processing.

3.3 Primary Processing

3.3.1 Crushing

Crushing is the first mechanical stage in the process of comminution in which the main objective is to reduce the rock particles to a size at which they can be subjected to grinding in tumbling mills. It is usually a dry operation and is performed in two or three stages. Lumps of run of mine ore can be as large as 1.5 m across and these are reduced in size to 10 - 20 cm in heavy duty machines. Primary crushers are commonly designed to operate 75% of the available time, mainly because of interruptions caused by insufficient crusher feed or by mechanical delays.

Secondary crushing includes all operations for reclaiming the primary crusher product from ore storage to the disposal of the final crushed product which has a normal size range of between 20 and 5 mm. The secondary crushing stage will usually consist of one or two size reduction stages with appropriate crushers and screens.

3.3.2 Grinding

Grinding is the last stage in the process of comminution. In this stage, the rock fragments are reduced in size by a combination of impact and abrasion, either dry or in a suspension in water. It is performed in cylindrical rotating steel vessels known as tumbling mills. These contain a charge of loose crushing bodies - the grinding medium - which is free to move inside the mill, thus comminuting the rock particles. The grinding medium may be steel rods, or balls, hard rock or in some cases the rock itself. In the grinding process particles between 5 and 250 mm are reduced in size to between 10 and 250 µm.

Although tumbling mills have been developed to a high degree of mechanical efficiency and reliability they are extremely wasteful in terms of energy expended, since the ore is mostly broken as a result of repeated, random impacts.

Grinding is usually performed wet, although in certain applications dry grinding is used. When the mill is rotated the mixture of medium, ore, and water, known as the mill charge, is intimately mixed, the medium comminuting the particles by impact or compression, chipping or abrasion. Most of the kinetic energy of the tumbling load is dissipated as heat and noise and only a small fraction being expended in actually breaking the particles.

Thus, for the purposes of this report it is assumed that the comminution process reduces the run of mine ore from a coarse, unsorted material, to a size fraction of approximately 100 µm which is suitable for the dissolution process described here. It should be noted that comminution is the most energy and cost intensive part of a mineral processing operation and that it is important to strike a balance between the minimum size fraction and cost.

3.4 Brine Extraction

The method dependent on a magnesium rich brine as the feedstock would require the pumping of approximately 1.4 M l/hr of brine to feed the sequestration plant. Data from CSMA experience is based on the costs from Geothermal Research and indicates that for a 2,200 m borehole a pressure drop of 10 Mpa can be reasonably expected at the wellhead for a 24 l/sec flow rate of brine produced.

Pumps operating at 80% efficiency will provide some 70,000 l/hr giving a total estimated number of pumps and production wells as 20. Much of the borehole and pump information comes from Harrison *et al* (1990).

Although this type of operation would be extremely large, modern pump technology is sufficient to meet the demand should the other constraints posed by the process be surmountable.

3.5 Conclusions

The open pit mining and primary processing of ultramafic rocks is analogous to many modern day industrial and metalliferous mining operations in that the scale of extraction and methods of size reduction are all well understood.

In terms of the total energy requirement for the sequestration process, the mining and primary processing generally represent a very small part of the energy balance, and as such, are not considered to be a major stumbling block for the silicate-based processes.

In contrast, the enormous pump capacity required to pursue the brine extraction method and probable re-injection of acid product, does create considerable problems over and above those posed by the chemical process itself.

4.0 CHEMICAL REACTIONS

4.1 Introduction

As has been described previously in Section 1, storage of CO_2 as $MgCO_3$ or $CaCO_3$ represents ways of safely sequestering CO_2. These carbonates are only sparingly soluble in water, are non-hazardous and furthermore, Mg and Ca are extremely abundant elements in the earth. However, there are questions relating to the effects of acid rain upon the carbonate products of the sequestration process. Rainwater, unaffected by sulphur or nitrogen oxides, is mildly acidic due to the formation of carbonic acid through reaction with atmospheric carbon dioxide. In reaction with $CaCO_3$ or $MgCO_3$ there are dissolution products of bicarbonate and metal ions. These may produce adverse environmental effects.

The reaction of sulphurous acid rain with limestone or dolomite produces carbon dioxide and a skin of insoluble calcium or magnesium sulphate. The susceptibility and rate of dissolution of the sequestration products will depend largely on the form and permeability of these products and should be tested at a pilot plant level. Storage areas may need to be lined/sealed to prevent ingress of rainwater and groundwater.

If these problems can be overcome, then sequestering CO_2 as stable carbonate minerals has none of the environmental concerns which attend the storage of CO_2 in aquifers or in the ocean where there is the possibility of a sudden release of CO_2 held in a metastable state.

Stable carbonates with large negative free energies of formation are formed by all the alkaline earth and lanthanide elements. However, of these, only Mg and Ca occur in sufficient abundance and concentration in the earth to be considered. It is well known (Greenwood and Earnshaw, 1986) that both these carbonates decompose at elevated temperatures losing CO_2, whilst it is also known that on a geologic timescale, weathering of Mg and Ca-rich igneous rocks has produced vast deposits of these sedimentary carbonates.

In addition, $CaCO_3$ is more thermally stable than $MgCO_3$, but this difference in stability is quite negligible considering that vulcanism readily liberates CO_2 from both sources. In contrast, the CO_2 sequestration process will only produce relatively small amounts of carbonate rock when compared with sediments made of these materials deposited over geological time.

Thus the choice of which metal to use comes down to its availability and ease of processing towards the carbonate.

4.2 Sources of Mg and Ca

By far the most common form of alkaline earth metal-rich non-carbonate rocks in the earth are silicates, so it is clear that if a rock source is to be used, it is likely that silicates would provide the feedstock. A major, and probably overwhelming, consideration is that, as Table 2.1 shows (Lackner *et. al.* 1995) and as has previously been pointed out (Lackner *et. al.*

1997), the Ca content of the Ca-rich sources is much smaller than the Mg content of the Mg-rich sources. Therefore, a Mg source will be advantageous from the point of view of the mass of rock which must be mined in order to sequester a particular amount of CO_2.

In addition to the Mg and Ca bearing silicates, magnesium-rich brines which contain $MgCl_2$ that could allow a shortened carbonation process, also represent a potential feedstock for CO_2 sequestration, whilst dolomite ($CaMg(CO_3)_2$) may also be considered. The geology and distribution of these various sources has been discussed in Section 2 of this report.

As an illustration of the potential sequestration properties of a number of oxides, hydroxides and silicates, Table 4.1 shows the theoretical mass or rock required per tonne of sequestered CO_2.

Table 4.1: Sequestering Properties of Various Chemical Phases

Material	Mass (g) of 1 mole of material	Molar ratio of CO_2 to rock	Mass (t) to sequester 1 t of CO_2
CO_2	44.0	-	-
Mg_2SiO_4	140.7	0.5	1.6
$MgSiO_3$	100.4	1.0	2.3
Ca_2SiO_4	172.2	0.5	2.0
$CaSiO_3$	116.2	1.0	2.7
$Mg_3Si_2O_5(OH)_4$	**277.1**	**0.33**	**2.1**
$Mg(OH)_2$	58.3	1.0	1.3
$Ca(OH)_2$	74.1	1.0	1.7
MgO	40.3	1.0	0.92
CaO	56.1	1.0	1.3

These are the best case values and assume that the rock is composed purely of the mineral and that there is no wastage of the mineral in conversion to the carbonate. The oxides tend not to occur naturally and the hydroxides only in small amounts, although brucite ($Mg(OH)_2$) is found in metamorphosed dolomites and as veins with calcite and talc in serpentinites (Read, 1971).

It is noticeable that the corresponding ratios for Ca are greater simply due to the fact that the Ca atom is heavier than the Mg atom. In addition, the greater the alkaline earth:silicon ratio the smaller the mineral:CO_2 mass ratio, thus rendering deposits rich in the alkaline earth elements as the prime targets.

For example, if one were to sequester all of the 3 Mt of CO_2 produced per year by a typical power plant using a pure Mg_2SiO_4 source of Mg, one would require approximately 5 Mt of rock to be mined and converted for CO_2 removal per year. These tonnages are well within the bounds of the modern extractive industries, but does assume that the product used is in pure form. In reality, impurities and process inefficiencies will certainly necessitate larger tonnages being mined than the calculations stipulate (see Section 7).

4.3 Thermodynamics

Chemical processes are characterised by a number of thermodynamic properties.

In a chemical equilibrium

$$\text{Reactants} \xrightarrow{\text{eqm}} \text{Products}$$

The enthalpy change of the reaction (ΔH) describes the amount of heat produced or consumed by the reaction (i.e. whether it is exothermic or endothermic). The entropy change (ΔS) describes the change in the "disorder" or number of degrees of freedom of the system. Together the enthalpy and entropy change define the Gibbs Free Energy change of the reaction (ΔG) according to:

$$\Delta G = \Delta H - T\Delta S$$

Where T is the absolute temperature (Kelvin scale) of the system.

The value of ΔG defines the equilibrium of the system according to

$$\Delta G = -RT \ln K_{\text{eqm}}$$

where K_{eqm} is the equilibrium constant of the reaction, indicating the amounts of reactants and products at the equilibrium point, and R is a universal constant called the Universal Gas Constant.

Clearly both ΔG and K_{eqm} are dependent on the temperature of the system.

The key point is that for a reaction to be thermodynamically feasible (i.e. to favour the products) ΔG, as defined above, must be negative. This corresponds to the situation in which the products lie in a lower energy state than the reactants.

Chemical compounds are defined in terms of Free Energies, enthalpies and entropies of formation from their constituent elements. Since there must be conservation of matter during the reaction, it is straightforward to calculate the characteristics of the reaction providing thermodynamic data exist for the constituent compounds on both side of the equilibrium.

4.3.1 Thermodynamics of Carbonate Formation

Consider the thermodynamics of producing carbonates from possible precursor solids. The thermodynamic data for Mg and Ca-containing solids are available as functions of temperature (Robie and Hemingway, 1995), and are corroborated elsewhere in the literature.

As described above, one can calculate easily the changes in enthalpy (ΔH) and Gibbs Free Energy (ΔG) associated with various possible processes for obtaining the carbonates.

For example, the process to convert Forsterite (Mg_2SiO_4) to $MgCO_3$ proceeds according to the following overall equation:

$$\underbrace{\tfrac{1}{2}\mathrm{Mg}_2\mathrm{SiO}_{4(s)} + \mathrm{CO}_{2(g)}}_{\Delta G_{f1}} \xrightarrow{\Delta G} \underbrace{\mathrm{MgCO}_{3(s)} + \tfrac{1}{2}\mathrm{SiO}_{2(s)}}_{\Delta G_{f2}}$$

Eqn 1

$$\Delta G_{f1} = \mathrm{Mg}_{(s)} + \tfrac{1}{2}\mathrm{Si}_{(s)} + \mathrm{C}_{(s)} + 2\mathrm{O}_{2(g)} \longrightarrow \tfrac{1}{2}\mathrm{Mg}_2\mathrm{SiO}_4 + \mathrm{CO}_2$$

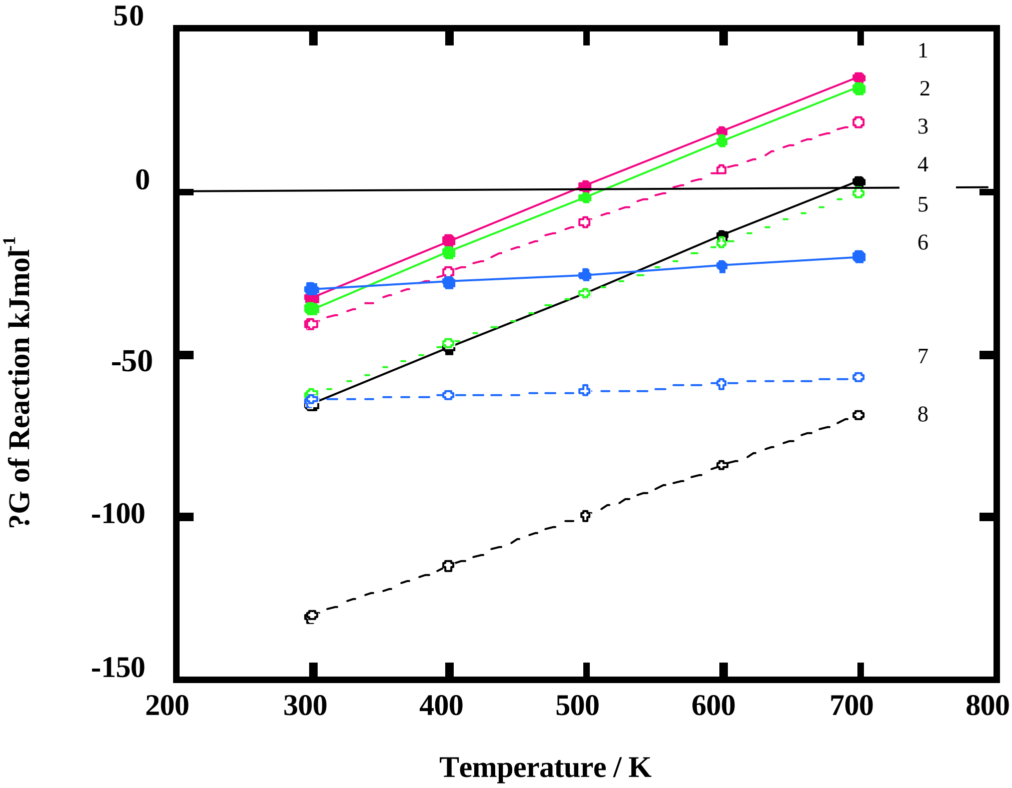
$$\Delta G_{f2} = \mathrm{Mg}_{(s)} + \tfrac{1}{2}\mathrm{Si}_{(s)} + \mathrm{C}_{(s)} + 2\mathrm{O}_{2(g)} \longrightarrow \mathrm{MgCO}_3 + \tfrac{1}{2}\mathrm{SiO}_2$$

$$\Delta G = \Delta G_{f2} - \Delta G_{f1}$$

In doing such a calculation at a particular temperature, we consider the free energies of formation of the compounds on both sides of the overall reaction at that temperature. The overall free energy of the reaction, ΔG, is simply the difference in the free energies of formation of the compounds on either side. Similar calculations can be applied to the enthalpy of reaction ΔH.

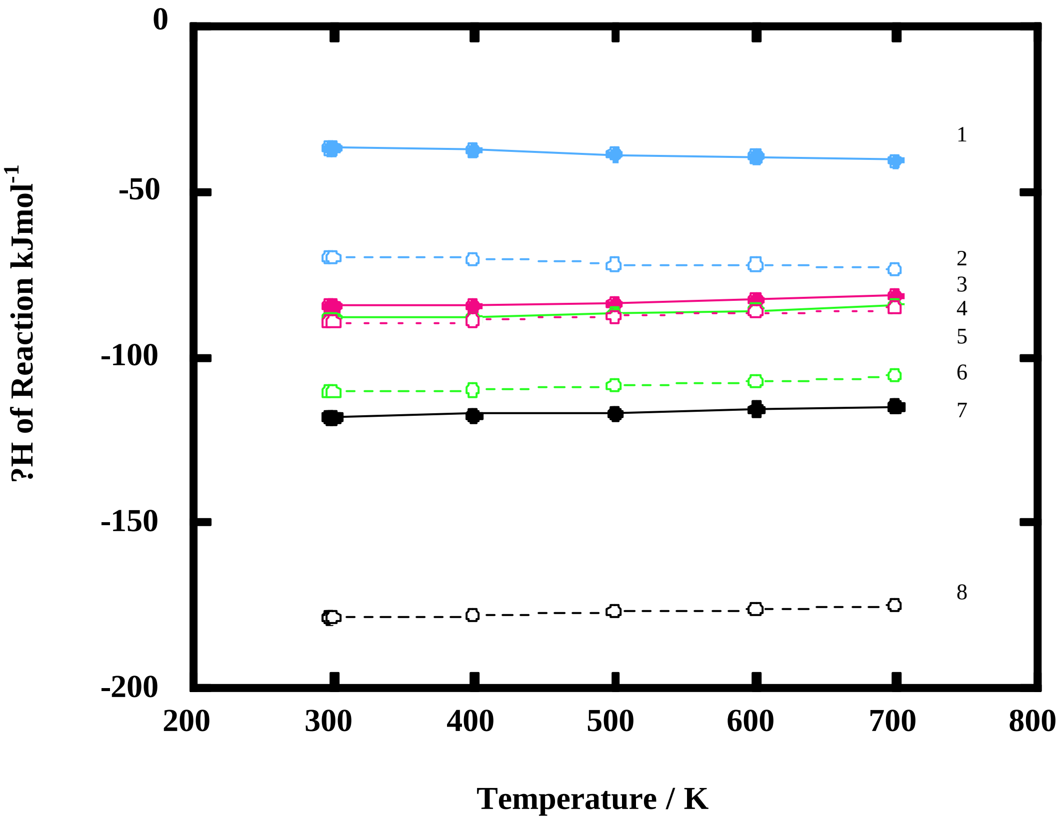
Figure 4.1 shows that for several solid sources of Mg and Ca as well as for the oxides and hydroxides (which occur rarely in nature) the reactions of the type in Eqn 1 are thermodynamically favourable particularly at low temperatures. Figure 4.2 shows the enthalpy changes for the same reactions.

With the exception of carbonation of the hydroxides, ΔG becomes less negative as temperature increases. This is because the gaseous reactant, CO_2 is favoured as temperature increases for entropic reasons ($\Delta G = \Delta H - T\Delta S$).



1. $MgSiO_3 + CO_2 = MgCO_3 + SiO_2$
2. $0.5 Mg_2SiO_4 + CO_2 = MgCO_3 + 0.5SiO_2$
3. $CaSiO_3 + CO_2 = CaCO_3 + SiO_2$
4. $MgO + CO_2 = MgCO_3$
5. $0.5Ca_2SiO_4 + CO_2 = CaCO_3 + 0.5SiO_2$
6. $Mg(OH)_2 + CO_2 = MgCO_3 + H_2O$
7. $Ca(OH)_2 + CO_2 = CaCO_3\ H_2O$
8. $CaO + CO_2 = CaCO_3$

Figure 4.1: Free energy change as a function of temperature for the reactions indicated. All gaseous species are assumed to be at a pressure of 1 atm.



1. $Mg(OH)_2 + CO_2 = MgCO_3 + H_2O$
2. $Ca(OH)_2 + CO_2 = CaCO_3 . H_2O$
3. $MgSiO_3 + CO_2 = MgCO_3 + SiO_2$
4. $0.5 Mg_2SiO_4 + CO_2 = MgCO_3 + 0.5SiO_2$
5. $CaSiO_3 + CO_2 = CaCO_3 + SiO_2$
6. $0.5Ca_2SiO_4 + CO_2 = CaCO_3 + 0.5SiO_2$
7. $MgO + CO_2 = MgCO_3$
8. $CaO + CO_2 = CaCO_3$

Figure 4.2: Enthalpy change as a function of temperature for the reactions indicated.

4.3.2 Kinetic factors

These simple thermodynamic calculations show that in principle the formation of carbonates from silicates is thermodynamically favourable. However, thermodynamic calculations cannot indicate whether a reaction will actually take place at a rate fast enough to be viable. All chemical reactions have an activation energy which must be surmounted in order to proceed from the reactants to the products. If the activation barrier is low, the rate of reaction will be fast, whereas if it is high, the reaction will occur only negligibly slowly, even if it is thermodynamically very favourable. The activation barrier is not closely correlated with the enthalpy or free energy change of the reaction.

Generally, thermal energy allows the activation barrier to be surmounted, so raising the temperature always increases the rate of chemical processes. Provision of an alternative reaction pathway with a lower activation barrier may be provided by a catalyst which will cause an increase in reaction rate at a particular temperature.

Most solid-gas reactions are slow. This is because the gas is only in direct contact with the small amount of solid which is exposed at the surface of the solid grains. Also the chemical bonds in the solid (and perhaps in the gas molecules) must be broken before the new, more stable, set of bonds can form. Often temperatures of several hundred degrees centigrade are required before reaction takes place at a reasonable rate.

Figure 4.2 shows that at the temperatures which will be required for the reaction of CO_2 with the naturally occurring silicate minerals, most are thermodynamically disfavoured for the reasons discussed in Section 4.3.1 above.

4.4 Carbonation of Mg or Ca Hydroxides.

The only compounds for which the thermodynamics are favourable even at elevated temperatures are $Ca(OH)_2$ and $Mg(OH)_2$. This is because there are equal numbers of gas molecules (CO_2 or H_2O) on either side of the equilibria relating to the carbonation of these two materials.

In the reactions under consideration, unless gas molecules occur on both sides of the chemical equilibrium, ?G becomes >0 at the sort of temperatures required for reasonably fast gas and solid reactions. Thus, only the $Mg(OH)_2 + CO_2$ and $Ca(OH)_2 + CO_2$ routes (flat lines in Figure 4.1) do not become thermodynamically disfavoured at high temperatures.

The ΔG for these reactions does not change significantly with temperature, for entropic reasons, and is reasonably favourable in the case of either Mg or Ca.

This reaction can be thought of as a simultaneous dehydration and carbonation of the hydroxide.

Eqn 2. $$Mg(OH)_{2(s)} + CO_{2(g)} \xrightarrow{eqm} MgCO_{3(s)} + H_2O_{(g)}$$

The calculations for Figure 4.2 assume partial pressures of all gaseous reagents of 1 atmosphere in the equation above. One could make ΔG even more negative in these cases by either increasing the pressure of CO_2 or decreasing the pressure of H_2O (for example by condensing the vapour produced in a heat exchanger).

Thus, treatment of the solid hydroxides with gaseous CO_2 at slightly elevated temperatures and/or at elevated pressures of CO_2 is a possible method for sequestering CO_2.

4.4.1 Carbonation of $Mg(OH)_2$

Butt *et al* (1996) have explored this possibility in the case of Mg and have published some data on the carbonation of $Mg(OH)_{2(s)}$ by CO_2. This is in addition to more recent work by these authors (Lackner *et al*, 1997; Wendt *et al*, 1998 and Lackner *et al*, 1998). The conclusions of these studies are not yet conclusive, primarily due to the number of variables in the process. However, it is instructive to consider the various findings which have been reached.

In their initial, published, study on the kinetics of the carbonation and dehydration of $Mg(OH)_2$ (Butt *et al*, 1996), they have established the following:

Using $Mg(OH)_2$ powder with an average grain size of 20 µm, they carried out reactions to investigate the dehydration and also the dehydration/carbonation of $Mg(OH)_2$. Using thermogravimetric analysis, TGA measurements and subsequent analysis of the products using X-ray powder diffraction, microscopy and reaction with acid, they established that $Mg(OH)_2$ dehydrates readily at 350°C and above, breaking up the particles to produce MgO. They established that under a pressure of CO_2 (estimated to be 0.5 atm for their measurements) there is simultaneous dehydration and carbonation. However, the formation of a carbonate crust hampers both the dehydration and the carbonation so the product consists of grains which are composed of an inner core of non-dehydrated hydroxide (and some oxide) and a crust of carbonate.

Their “best” result was obtained with exposure to the CO_2 atmosphere for 12 hours at 375°C followed by cooling at 20°C per minute to room temperature with subsequent chemical analysis.

In this case, chemical analysis carried out by dissolving the material in acid and measuring the amount of CO_2 produced from the carbonate present revealed that the sample consisted of 16.7% by mass of $MgCO_3$. Their X-ray diffraction measurement of the product of this reaction shows that MgO and $Mg(OH)_2$ are present in roughly a 1:1 ratio.

A simple calculation reveals that the composition of the product is roughly $(MgCO_3)_{0.1}(Mg(OH)_2)_{0.4}(MgO)_{0.5}$. This means that 1 mole of $Mg(OH)_2$ derived from 1 mole of silicate rock will only sequester about 0.1 moles of CO_2 (primarily a result of the formation of the carbonate crust which protects the hydroxide from further carbonation). This being the case, it would increase by a factor of 10 the amount of $Mg(OH)_2$ which would be required and hence the amount of Mg-containing rock which would have to be mined. For example 16 t of Mg_2SiO_4 would be required for the sequestration of 1 t of CO_2.

If we consider the technical implications for the large scale process, assuming that the actual carbonation is carried out in a similar manner to the experiments of Butt *et al* (1996), their highest degree of carbonation was achieved when the reaction was carried out at 375^oC. This resulted in the production of 0.1 mole fraction of carbonate after 12 hours exposure to CO_2.

Thus, in order to sequester all the CO_2 from a power station (3 Mt per year assumed), one needs to sequester approximately 4000 t in 12 hours. Thus, the minimum amount of $Mg(OH)_2$ which would be required is 5,200 t, and if the reaction is only 10 % efficient, the amount of $Mg(OH)_2$ required in a 12 hour period would be 52,000 t. Furthermore this vast amount of material must be heated to a temperature of 375^oC.

After the reaction has taken place, the product (again of the order of 50,000 t according to the TGA measurements of Butt *et al*, 1996) must be removed from the reactor in order that replenishment can take place.

Of course, the hydroxide must be in a form that makes it reactive to CO_2 gas. Clearly if the $Mg(OH)_2$ powder is densely packed, it will not be reactive. It must be present as a finely divided and "fluffed up" powder. Assuming that this might have a density of 2 t/m^3 which is a typical value for a finely divided hydroxide, although perhaps a little on the high side, the volume of material required during a 12 hour carbonation cycle is over 25,000 m^3, assuming the 10% efficiency for the carbonation.

In consideration of some of the CO_2 sequestration reactions, it has been suggested that the heat released by the exothermic reaction will help to maintain the reaction at an elevated temperature if this is required. As can be seen from the graph in Figure 4.2 for the case of carbonation of finely divided $Mg(OH)_2$, the enthalpy change for the reaction is about -40 $kJmol^{-1}$ at 375^oC. Assuming that the reaction is about 10% efficient (Butt *et al*, 1996), then 4 kJ of heat energy will be produced per mole of $Mg(OH)_2$ starting material.

The heat capacity of $Mg(OH)_2$ is about 100 $JK^{-1}mol^{-1}$, and thus the heat produced in the reaction would be sufficient to raise the temperature of the hydroxide by up to 40 K. This of course assumes that the heat energy was supplied all at once to the hydroxide.

The results of Butt *et al* (1996) show that the 10% efficiency of the reaction is achieved after exposure to CO_2 for 12 hours. The heat released by the reaction will be produced over this time period and there will inevitably be considerable losses. Thus, it is clear that the reaction cannot be used to heat itself, but that an external heat source is required to raise the temperature of the hydroxide to the working temperature.

It should be noted that in the very best scenario of 100% conversion of the hydroxide to the carbonate, assuming the reaction takes place over a much shorter time scale (say 1-2 hours), then there would be a very significant contribution from the reaction to the energy requirements of the process. This concept is considered further below.

As an example, assuming a process only 10% efficient, this would require 52,000 t of $Mg(OH)_2$ which corresponds to 8.9×10^8 moles. The heat capacity of this is 100 $JK^{-1}mol^{-1}$, so to raise the temperature from 25°C to 375°C requires 35 $kJmol^{-1}$.

Thus to heat one "12 hour batch" of $Mg(OH)_2$ requires 3.1×10^{10} kJ of energy assuming there are no losses to the environment.

One obtains 394 kJ from the combustion of 1 mole of carbon to produce 1 mole of CO_2

So the process to sequester a "12 hour batch" of CO_2 (4000 t) requires 7.9×10^7 moles of carbon to be burnt in order to heat the hydroxide. This corresponds to 950 t of C and will produce 3500 t of CO_2 assuming that all the heat energy comes form the burning of a fossil fuel source. The small contribution from the exothermic reaction has been ignored here as have any losses: i.e., it is assumed that no additional energy is required to maintain the hydroxide at 375°C.

This shows that roughly speaking, sequestration of CO_2 by this method will, according to

This analysis has concentrated on the situation in which the reaction is processed in a batch mode. In reality a flow type system will be used, but this will not change the fundamental thermodynamic properties of the system.

Of course there are various ways in which the thermodynamics and kinetics of the process might be improved:

- Use smaller particles of $Mg(OH)_2$ in the carbonation process. This would speed the reaction by offering a larger surface area to the CO_2 and would also decrease the size of the unreacted hydroxide core giving a larger $MgCO_3$:$Mg(OH)_2$/MgO ratio in the final product.

- Use an increased pressure of CO_2. This is likely to be the conditions in which the CO_2 is supplied from the power plant to the sequestering site. This would improve the amount of conversion and should have the effect of speeding up the reaction through more collisions of CO_2 molecules with a reactive surface.

If the two improvements above are adopted, this will enable more of the heat required to maintain and attain the reaction temperature to be supplied by the reaction itself.

Completely dehydrate the hydroxide, producing finely divided MgO which may be more reactive to CO_2. However, this would require a temperature of between 400 and 500^{o}C according to the dehydration measurements of Butt *et al* (1996). Indeed, recent results of Wendt *et al* (1998(b)) suggest that MgO does not carbonate very rapidly and that its formation is actually disadvantageous.

In the light of the work by Butt *et al* (1996), this solid + gas reaction seems to be too sluggish at ambient temperature and pressure despite being thermodynamically attractive. However, in view of the fact that almost no work has been done to investigate the process in detail, there should be further studies devoted to this in addition to pilot plant investigations.

More recent studies (Lackner *et al*, 1998) by the same team have established that the carbonation of $Mg(OH)_2$ proceeds rapidly at 400 - 500^{o}C and at pressures of CO_2 of about 6 atmospheres in about 30 minutes using finely divided $Mg(OH)_2$ which is obtained as a precipitate - a different starting hydroxide from the commercial material used in their initial study. However, these claims are not backed up with any data. Indeed even more recent work seems to contradict this (Wendt *et al*, 1998(b)).

Assuming that this enhancement to full efficiency is possible, the feasibility of the process rises dramatically:

On the 12 hour time-scale for the treatment of 4000 t of CO_2, one now requires just 5200 t of $Mg(OH)_2$ and this could in principle just about be raised to the operating temperature by the heat of reaction assuming no losses. This conclusion is in contrast with the conclusions of Lackner *et al* (1997) who state that there would actually be a very significant power output from this process. Indeed they state that the power output from this process will be 513 MW based on the reaction of 32,000 t of $Mg(OH)_2$ per day. In fact the enthalpy of reaction and the heat capacity of the $Mg(OH)_2$ suggest that the amount of energy actually produced by the carbonation will be 255 MW on this scale and that all this will be required to heat the material in the reaction vessel.

However, this analysis leads us to suppose that if the additional energy input into the process is relatively small then it may be feasible in practice. The analysis above shows just how sensitive the process is to the conditions under which it is carried out.

The description above has focused on the actual $Mg(OH)_2$ + CO_2 solid/gas reaction which may be feasible albeit not very efficient. One also has to consider the production of large quantities of $Mg(OH)_2$ from a suitable Mg source such as a magnesium-rich silicate. Wendt *et al* (1998(c)) have done a considerable amount of work in the area of $Mg(OH)_2$ production. The conclusion from their work is that the dissolution of the silicate rock in HCl followed by the eventual precipitation of $Mg(OH)_2$ requires too much energy to be supplied in order to evaporate the vast quantities of water used in order to reclaim the HCl.

This acid dissolution of silicate rock is based on the following process:

$$\tfrac{1}{2}\mathrm{Mg_2SiO_{4(s)}} + 2\mathrm{HCl_{(aq)}} \xrightarrow{\text{eqm}} \mathrm{MgCl_{2(aq)}} + \tfrac{1}{2}\mathrm{SiO_{2(s)}} + \mathrm{H_2O_{(l)}}$$

$$\mathrm{MgCl_{2(aq)}} \xrightarrow{\text{heat}} \mathrm{MgCl_2}.n\mathrm{H_2O_{(s)}} \xrightarrow{\text{heat}} \mathrm{MgCl(OH)_{(s)}} + \mathrm{HCl_{(g)}} + (n-1)\mathrm{H_2O_{(g)}}$$

$$2\mathrm{MgCl(OH)_{(s)}} + \mathrm{H_2O_{(l)}} \longrightarrow \mathrm{Mg(OH)_{2(s)}} + \mathrm{MgCl_{2(aq)}}$$

The $Mg(OH)_2$ and SiO_2 are removed as solids from the process and the $MgCl_{2(aq)}$ produced in the final process is recycled into the second step. It is the second step which is very energy intensive as it involves dehydration of the $MgCl_2$.

4.4.2 Silicate Dissolution in Hydrated $MgCl_2$

Recently, Wendt *et al* (1998; 1998(a); 1998(b); 1998(c)) have considered a new process designed to produce $MgCO_3$ from Mg silicate avoiding the use of a laborious and very energy intensive process described above for making $Mg(OH)_2$.

The idea here is to avoid the use of vast quantities of water by dissolving the rock in an acidic melt of hydrated $MgCl_2$ and then either obtaining $Mg(OH)_2$ which is carbonated in a second step (as in 4.4.1 above) or by carbonating the melt directly to obtain the carbonate and vastly simplifying the process.

This is currently the focus of research by the group of Wendt *et al.* These authors stress however that their analysis is only of the thermodynamics of the process and that actual experiments on a small scale will be required before it is clear whether this process is even feasible, let alone economic, for the sequestration of CO_2.

In their analyses there is a recognition that much of the heat from any exothermic processes may be lost and will not be available to some of the endothermic processes which are involved. It is likely that the actual situation may be worse than they suppose and that the sequestration may consume so much energy that, were it to be generated from fossil fuels, it would produce a large fraction of the amount of CO_2 which could be sequestrated. In particular, an assumption is made in some of their work (Lackner *et al*, 1997) that the $Mg(OH)_2$ carbonation will be exothermic enough to supply some heat to the overall process. In contrast, the analysis above indicates that it will not even be able to supply its own energy needs.

The simplest method which has been investigated here in terms of involving a relatively small number of steps is the following:

$$\tfrac{1}{3}\mathrm{Mg_3Si_2O_5(OH)_{4(s)}} + \mathrm{CO_{2(g)}} + \mathrm{MgCl_2(H_2O)_{n(l)}} \xrightarrow{\text{eqm}} \mathrm{MgCO_{3(s)}} + 2\mathrm{HCl_{(aq)}} + (n-1)\mathrm{H_2O_{(l)}} + \tfrac{1}{3}\mathrm{Mg_3Si_2O_5(OH)_{4(s)}}$$

$$\mathrm{MgCO_{3(s)}} + 2\mathrm{HCl_{(aq)}} + (n-1)\mathrm{H_2O_{(l)}} + \tfrac{1}{3}\mathrm{Mg_3Si_2O_5(OH)_{4(s)}} \xrightarrow{\text{eqm}} \mathrm{MgCO_{3(s)}} + \mathrm{MgCl_2(H_2O)}_{n+\frac{2}{3}(l)} + \tfrac{2}{3}\mathrm{SiO_{2(s)}}$$

However it is certainly not clear that these equilibria favour the formation of the carbonate and in any case a large pressure of CO_2 will be required to force the equilibrium over in favour of the carbonate. This is particularly because the activities of the CO_2 and HCl species in the melt are not known (Wendt *et al*, 1998(b); 1998(c)).

A more promising version of this still involves the method for preparation of $Mg(OH)_{2(s)}$, but stops at the point at which MgCl(OH) is generated. The concept is that this is then carbonated directly:

$$2\mathrm{MgCl(OH)} + \mathrm{CO_2} \longrightarrow \mathrm{MgCO_3} + \mathrm{MgCl_2} + \mathrm{H_2O}$$

These authors also indicate that a pressure of CO_2 of 10-20 atm will be required to drive this equilibrium in favour of the products. Further experimental studies of these various processes will be required before firm conclusions can be reached.

4.4.3 Reaction of CO_2 with lime water (aqueous $Ca(OH)_2$)

In the case of $Ca(OH)_2$, one can also consider the possible reaction of CO_2 with an aqueous Ca species:

$$\mathrm{Ca(OH)}_{2\mathrm{(aq)}} + \mathrm{CO}_{2\mathrm{(g)}} \longrightarrow \mathrm{CaCO}_{3\mathrm{(s)}} + \mathrm{H_2O}_{\mathrm{(l)}}$$

$$\mathrm{Ca(OH)}_{2\mathrm{(aq)}} \xrightarrow{\mathrm{eqm}} \mathrm{Ca}^{2+}_{\mathrm{(aq)}} + 2\mathrm{OH}^{-}_{\mathrm{(aq)}}$$

$$K_{\mathrm{sp}} = \frac{a_{\mathrm{Ca}^{2+}}\, a^{2}_{\mathrm{OH}^{-}}}{a_{\mathrm{Ca(OH)_2}}}$$

Where K_{sp} is the solubility product of $Ca(OH)_2$.

The activities, a, of solids are equal to 1 and those of the solution species may be approximated by their concentrations:

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{OH}^{-}]^{2}$$

The calcium and magnesium hydroxides and carbonates are all sparingly soluble. Table 4.2 defines the solubility products for each of these materials.

Table 4.2: Solubility Products of Selected Materials

Compound	K_{sp} / mol^{3}dm^{-9}
$Ca(OH)_2$	4.7 10^{-6}
$CaCO_3$	5.0 10^{-9}
$Mg(OH)_2$	5.6 10^{-12}
$MgCO_3$	6.8 10^{-6}

Thus, the saturation concentration of $Ca(OH)_2$ is 0.0167 mol dm^{-3}. $CaCO_3$ formed from such a saturated solution by passing CO_2 through it will precipitate out because it is less soluble. It is clear that this route is not appropriate in the case of Mg since the hydroxide is much less soluble than the Ca analogue and furthermore magnesium carbonate is actually more soluble than magnesium hydroxide.

The reaction of CO_2 bubbled through a saturated $Ca(OH)_2$ solution is familiar as the "CO_2 turns lime-water milky" reaction in elementary chemistry studies.

This method does not seem to have been considered by sequestration workers. One problem is that the low solubility of $Ca(OH)_2$ means that vast volumes of water will be required for the process to work on the desired scale. Furthermore, the relatively low Ca content of even the more Ca-rich rocks and the larger mass of Ca compared to Mg means that larger quantities will have to be mined than in the cases involving Mg.

An example of this process might proceed as:

At saturation [Ca^{2+}] = 0.0167 mol dm^{-3}. Therefore, since the mass of 1 mole of $Ca(OH)_2$ = 74.1 g, there will be about 1.2 g of $Ca(OH)_2$ in 1 litre (dm^3) of water, so one can sequester 0.7 g of CO_2 in 1 dm^3 of water.

Thus a tank of water 100 m × 100 m × 1 m = 10^7 dm^3 and would sequester 7 t of CO_2. The carbonate may then be removed by filtration and the water recycled. In order to sequester 3 × 10^6 t per annum (assumed power station output), it would be necessary to react all the $Ca(OH)_2$ in the tank described above with CO_2 in 1.2 minutes.

The reaction of CO_2 with limewater is fast, however, the implication is that the filtration and subsequent recharging of the water with $Ca(OH)_2$ would have to take place on a similar time-scale (assuming this was all the water that was used in the process). This would require a vast pumping capacity with a large energy requirement.

Although this method has the advantage of being carried out a room temperature (i.e. there is no need to heat the water) and will give full conversion (in contrast to the method of $Mg(OH)_{2(s)}$ + $CO_{2(g)}$) it seems as though the problem of the relatively low solubility of $Ca(OH)_2$ will make this non-viable. Due to the low concentration of the reactants, the energy produced will simply have a gentle heating effect on the water. It is unlikely that the heat of this reaction can be harnessed.

As in the case considered above for $Mg(OH)_2$, the vast amounts of $Ca(OH)_2$ required will need to be obtained from Ca-rich silicate rocks by a suitable process. However, a further complication arises in that the huge volumes of water required for the process cannot be sourced from the sea, as the natural $[Ca^{2+}]$ of seawater will cause the solubility product of the hydroxide to be exceeded at low $[OH^-]$.

4.5 Reaction of CO_2 with Carbonate/Chloride Mix

As an alternative approach, and one which strangely uses a carbonate (dolomite) as a starting product, the Weldon Process, which was first formulated in 1866, has also been considered. The process has been recently modified by Robertson (1995), but in essence, utilises the following reaction:

$$MgCO_{3(s)} + 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)} \xrightarrow{eqm} MgCl_{2(aq)} + 2NaHCO_{3(s)}$$

The process is based on the dissolution of $MgCO_3$ from dolomite in seawater, which is reacted with CO_2 at 10 atm to produce $MgCl_2$ and $NaHCO_3$ in solution, the latter being precipitated by large amounts of NaCl from a store (either mined or obtained from a massive desalination process). The solid $NaHCO_3$ and the $CaCO_3$ (undissolved component of the dolomite) are removed, whilst the NaCl in the NaCl/$MgCl_2$ solution is removed by evaporation. The excess NaCl and $MgCl_2$ can be disposed of into the sea, whilst the solids can be stored.

A potential drawback of the process is that $NaHCO_3$ is soluble and will leach out of the stored waste material.

Although the reactions operate at room temperature and a 10 bar CO_2 pressure is necessary, it is thought that the extremely large tonnages of NaCl required in combination with the huge volumes of liquids necessary for the reactions may well render the process inefficient and impractical.

4.6 Conclusions

A number of methods have been proposed or can be envisaged for the sequestration of CO_2 by forming alkaline earth carbonates from alkaline earth silicates and other potential feeds which are abundant in the geological world.

It appears that direct carbonation of the solid silicate, although thermodynamically favourable at low temperatures, is not so at the elevated temperatures which would be required for this type of reaction to be practical because it is kinetically slow. Indeed this method has not been considered as viable in the context of a flue gas treatment plant. It may be possible for CO_2 injection into the crust at high pressure to sequester CO_2 on a geological time scale, but this is beyond the scope of this study.

The carbonation of solid $Mg(OH)_2$ at elevated temperatures is thermodynamically favourable and has been shown to work at a reasonable rate and yield, although the energy which must be input into this process for a given amount of CO_2 represents a significant fraction of that which originally produced the CO_2.

In order to make the $Mg(OH)_2$ in the first place from a variety of magnesium silicate rocks (most notably serpentine and forsterite) by dissolution with HCl, and more directly from magnesium-rich brines, a significant amount of energy must be supplied.

To try and circumvent this procedure, Wendt *et al* (1998) have recently proposed variants in which a variety of Mg species are carbonated in a $MgCl_2$ melt (the $MgCl_2$ is recycled). Their thermodynamic studies of the various processes have established that overall, the best one can hope for, is that the process will consume roughly 160 kJ per mole of CO_2 sequestered. This is about 40% of the energy which can be produced by burning 1 mole of carbon to make 1 mole of CO_2. This ignores the cost in energy terms of mining and transporting the mined silicates.

In addition, it is a fact that high pressure will undoubtedly favour many of these reactions, but at the present time, lack of real experimental data precludes exploring this issue further.

In conclusion, a number of possible chemical reactions can be demonstrated to be amenable to the sequestration of CO_2, although it is only from a more detailed examination of each of the processes in terms of their efficiency, cost, confidence, public acceptance and applicability, that a preferred method can be chosen. Section 5 presents the available data for each suggested process.

5.0 PROCESS OPTIONS

5.1 Introduction

From the information presented in Section 4 which considered the chemistry of the potential reaction routes for CO_2 sequestration, six potential process options have been considered:

- Method 1 – Reaction with magnesium hydroxide produced from dissolution of a suitable magnesium-rich silicate rock;
- Method 2 – Reaction with magnesium hydroxide produced from dehydration of magnesium-rich brine;
- Method 3a – Reaction with magnesium hydroxide produced from dissolution of magnesium silicate rock in magnesium chloride melt;
- Method 3b – Direct carbonation from dissolution of magnesium silicate rock by magnesium chloride melt;
- Method 4 - Reaction with calcium hydroxide produced from dissolution of a suitable calcium-rich silicate rock, and
- Method 5 – Reaction of pressurised CO_2 with seawater-dissolved dolomite.

The aim of this section is compare these various processes and to determine the most appropriate for a full financial and technical appraisal.

Unfortunately, because of the youth of this area of research, there is a serious lack of material concerning actual experimental data on some of the more recently proposed processes. This means that while these can be quite readily examined from a thermodynamic point of view, it is much more difficult to establish which of these processes will be most efficient from a kinetic point of view. Consequently, it is not feasible to estimate a meaningful CO_2 balance for the processes not studied in detail.

For example, as indicated in Section 4, the direct carbonation of magnesium and calcium silicates is actually thermodynamically favourable at temperatures below a few hundred degrees. However, these reactions proceed only on a geological time scale (and in any case not by direct CO_2 + silicate reaction) in the weathering of igneous rocks. Increasing the temperature to the range of kinetic viability actually renders these direct reactions thermodynamically unfavourable. So, there are clearly a number of factors which need to be considered in the analysis.

To fully assess the viability of the six process options, and to ultimately select the most appropriate method, it is necessary to assess and compare a number of key decision factors relevant to the project:

- Efficiency of reaction;
- Cost;
- Confidence in process;
- Acceptance, and
- Overall applicability.

These five main areas can be further broken down using assessment criteria in a form as depicted in Figure 5.1. However, more detail is required than can be shown on a single figure, and thus each process will be described in a similar manner to allow comparisons to be made and data omissions highlighted. In particular, environmental issues will be discussed in more detail in Section 6.

In addition, a schematic flowsheet is presented for each method which highlights the main reactions and typical throughputs for an idealised one hour production cycle. This cycle time was chosen to represent a realistic and practical residence time for the main carbonation reaction in each of the processes.

It should be noted that the parameters used in this preliminary comparison have been chosen as best estimates, and are not necessarily those used for the detailed analysis described in Sections 7 and 8 of this report.

5.2 The Processes

5.2.1 Method 1

A. Efficiency of Reaction:

Description: Mine and crush a typical Mg silicate rock which has been assumed to contain up to 10% Fe oxides, 41% SiO_2 and 35% MgO. Dissolve rock in HCl, convert to powdered hydroxide, react with CO_2, dispose of $MgCO_3$, SiO_2 and bi-products. Figure 5.2 illustrates the main reaction stages and hourly tonnages, whilst Figure 5.3 presents the summary information for the process.

Equations:

Dissolution

$$\mathrm{MgFe_{0.13}Si_{0.78}O_{2.71}.0.95H_2O_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + 0.1FeCl_{2(aq)} + 0.03FeCl_{3(aq)} + 0.78SiO_{2(s)} + 1.95H_2O_{(l)}}$$

Dehydration

$$\mathrm{MgCl_{2(aq)} + H_2O_{(l)} \xrightarrow{\text{-H}_2\text{O of solution}} Mg(OH)Cl_{(s)} + HCl_{(g)}}$$

Repartitioning of Mg(OH)Cl

$$\mathrm{2Mg(OH)Cl_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + MgCl_{2(aq)}}$$

Carbonation

$$\mathrm{Mg(OH)_{2(aq)} + CO_{2(g)} \xrightarrow{\text{CO}_2\text{ 20 bar}} MgCO_{3(s)} + H_2O_{(g)}}$$

Mass flow: Solid starting materials and solid/slurry products only. Examples of various rock types are given in Table 5.1.

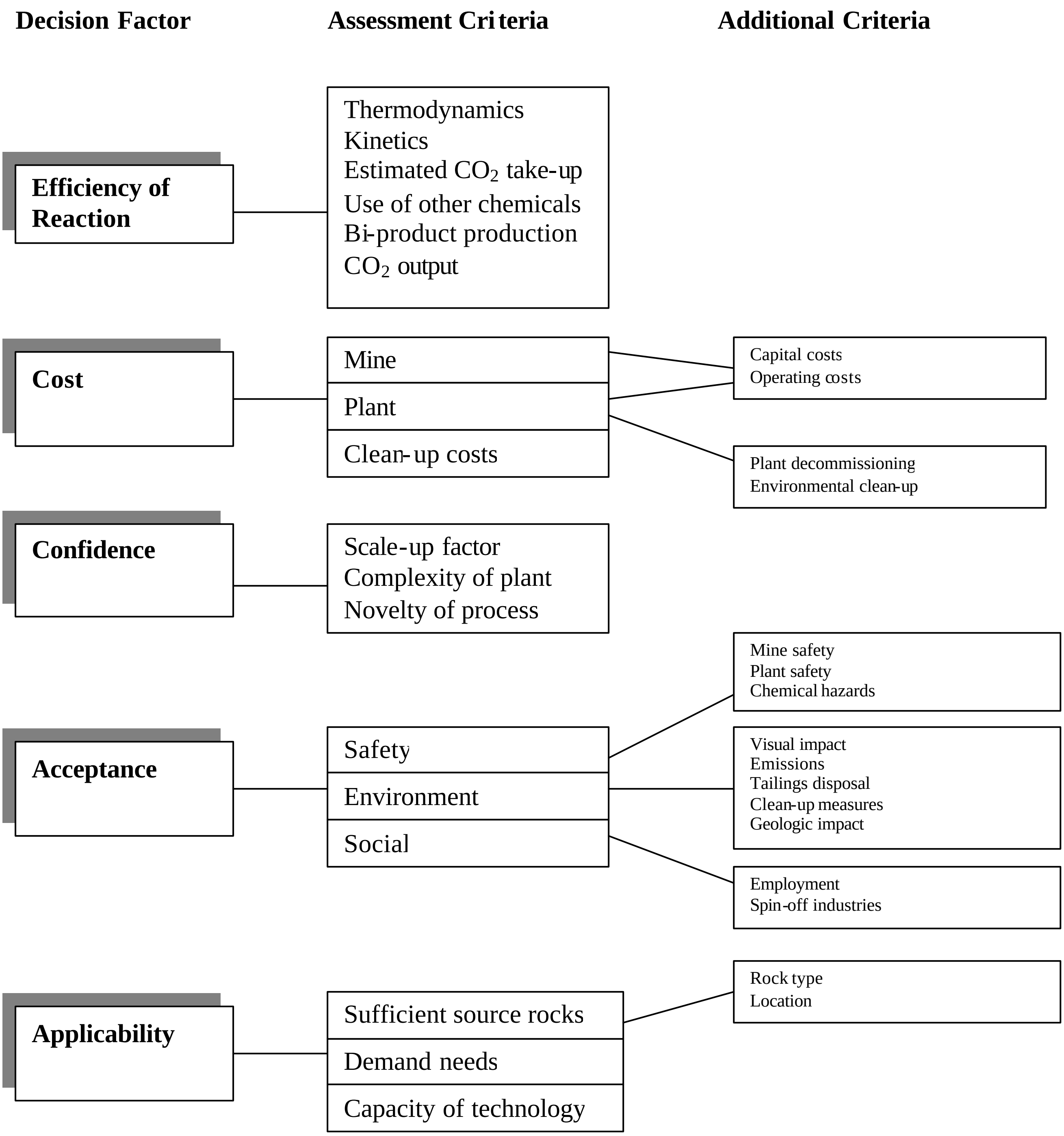


Figure 5.1: Decision tree for the comparison of selected sequestration methods.

Figure 5.2: Flowsheet for Method 1 (tonnages per hour)

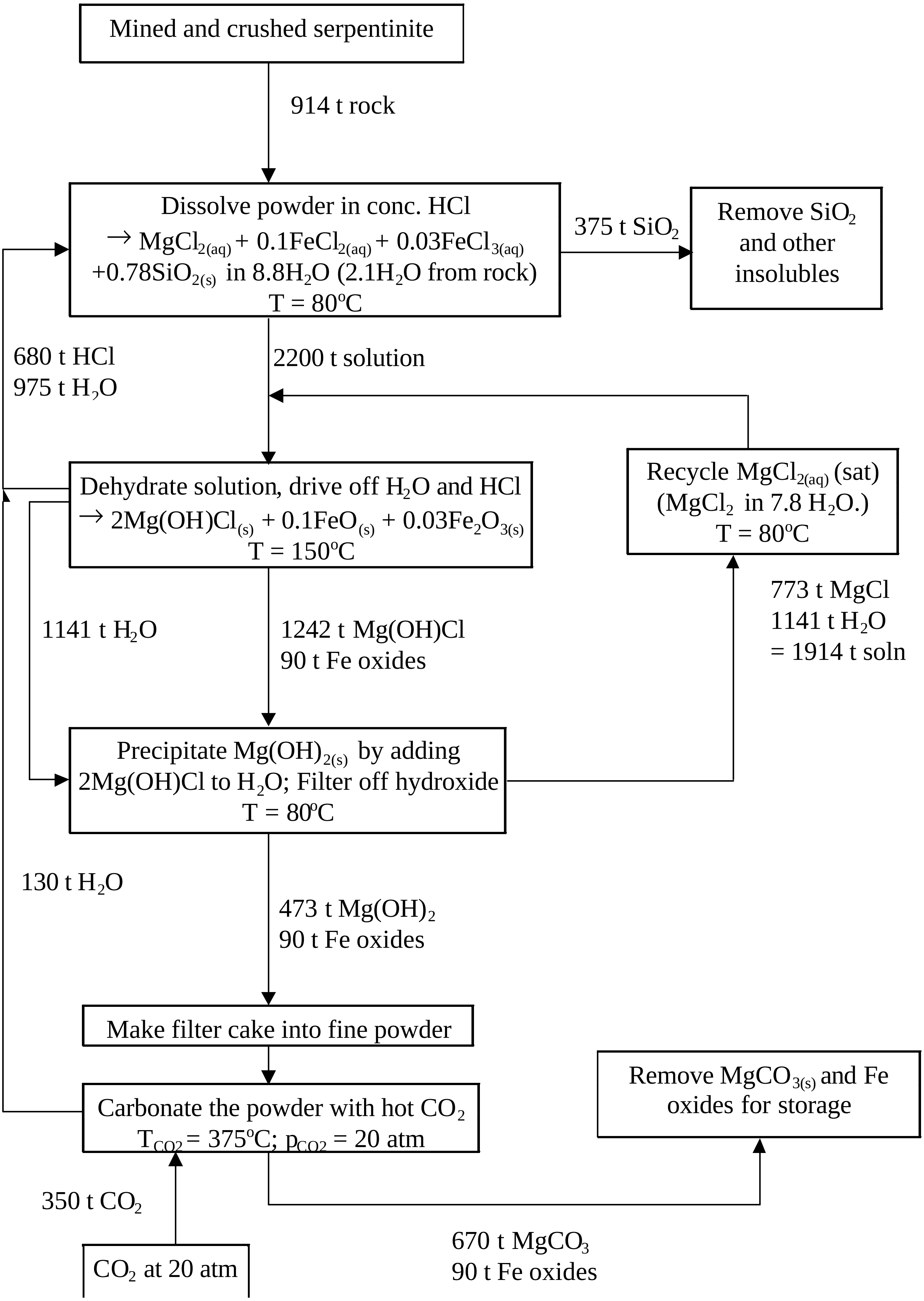
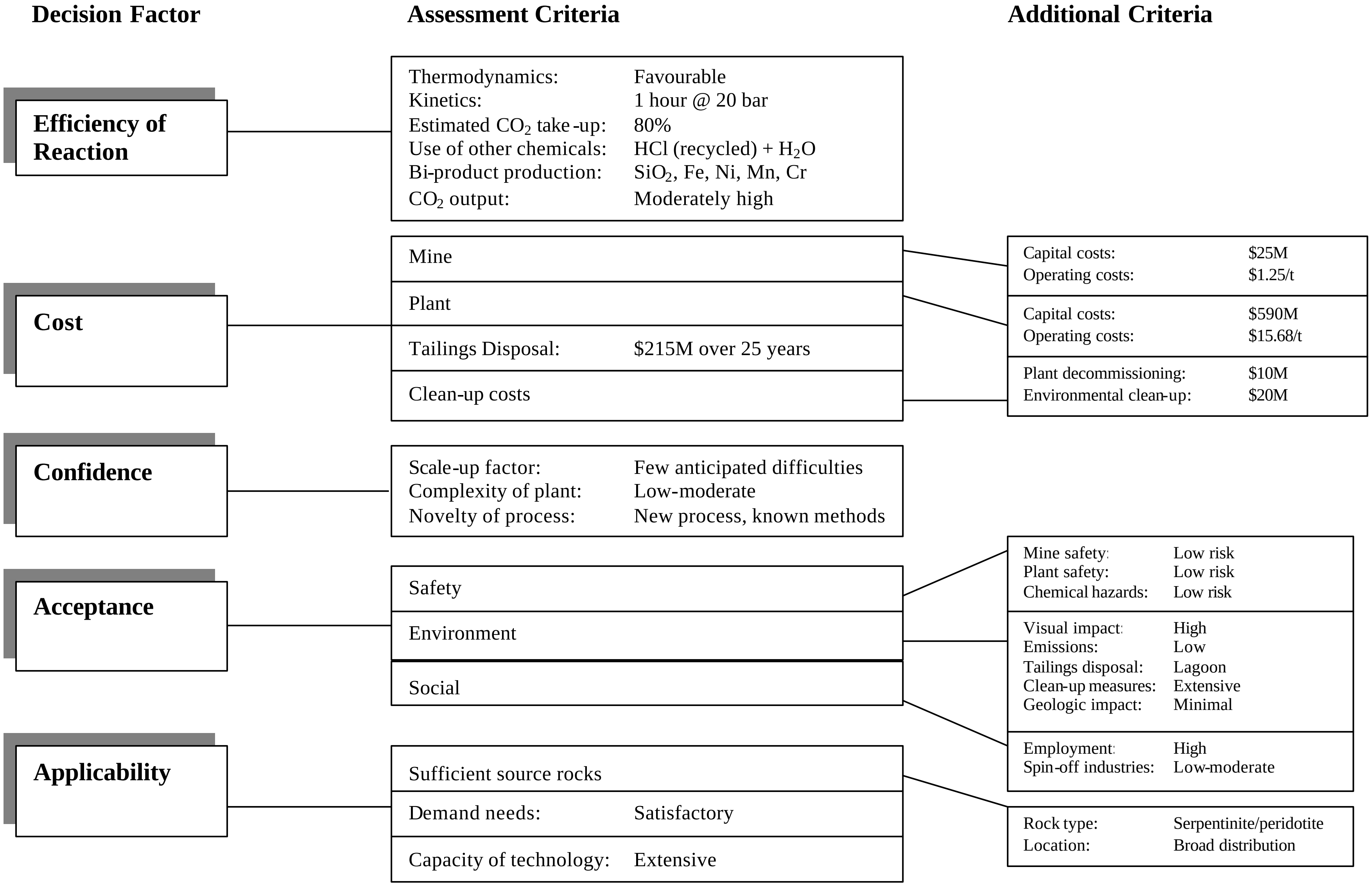


Figure 5.3: Method 1 – Dissolution of Magnesium Silicate-rich Rock



Decision Factor

Assessment Criteria

Additional Criteria

Efficiency of Reaction

Thermodynamics: Favourable
Kinetics: 1 hour @ 20 bar
Estimated CO_2 take-up: 80%
Use of other chemicals: HCl (recycled) + H_2O
Bi-product production: SiO_2, Fe, Ni, Mn, Cr
CO_2 output: Moderately high

Cost

Mine
- Capital costs: $25M
- Operating costs: $1.25/t

Plant
- Capital costs: $590M
- Operating costs: $15.68/t

Tailings Disposal: $215M over 25 years

Clean-up costs
- Plant decommissioning: $10M
- Environmental clean-up: $20M

Confidence

Scale-up factor: Few anticipated difficulties
Complexity of plant: Low-moderate
Novelty of process: New process, known methods

Acceptance

Safety
- Mine safety: Low risk
- Plant safety: Low risk
- Chemical hazards: Low risk

Environment
- Visual impact: High
- Emissions: Low
- Tailings disposal: Lagoon
- Clean-up measures: Extensive
- Geologic impact: Minimal

Social
- Employment: High
- Spin-off industries: Low-moderate

Applicability

Sufficient source rocks
- Rock type: Serpentinite/peridotite
- Location: Broad distribution

Demand needs: Satisfactory

Capacity of technology: Extensive

Table 5.1: Sequestering Properties of a Variety of Pure Minerals

Starting rock	**Mass of rock (t) required to store 1t CO_2**	Mass of product (t) for each 1t of CO_2			Mass of product (t) for each 1t of silicate rock		
		$MgCO_3$/t	SiO_2/t	**Total/t**	$MgCO_3$/t	SiO_2/t	**Total/t**
Forsterite Mg_2SiO_4	**1.6**	1.9	0.7	**2.6**	1.2	0.43	**1.63**
Serpentine $Mg_3Si_2O_5(OH)_4$	**2.1**	1.9	0.9	**2.8**	0.91	0.43	**1.34**
Olivine $MgSiO_3$	**2.3**	1.9	1.4	**3.3**	0.84	0.60	**1.64**

The information given in Table 5.1 above applies to any route which employs Mg containing starting rock, assuming that the rocks are purely composed of the mineral types listed in the first column. The numbers in the bold columns should all be as low as possible - thus the more Mg-rich rocks are favoured - although the availability of these is likely to determine which is used.

Thermodynamics I - heat flow: Need to consider the energy flows for the processes per tonne of CO_2 sequestered (= 2.3×10^4 moles).

i. Extraction of $Mg(OH)_2$:
Net energy requirement for all steps prior to carbonation (Lackner *et. al.* 1998) is 1.3×10^5 kJ per tonne CO_2, therefore energy required here, mainly associated with evaporation of water.

ii. Carbonation of $Mg(OH)_2$ at 375 ^oC:

Energy released:	9.1×10^5 kJ per tonne CO_2
Energy required to reach reaction temp:	7.9×10^5 kJ per tonne CO_2

As the carbonation process is almost energy neutral, one cannot rely on any energy input from the carbonation process to the extraction process. This is the best case scenario which assumes no energy losses. Note that this assumes that all the heat energy required to evaporate off the HCl and H_2O is returned to the system, which in practical terms, is unlikely.

The best case represents using 1.5% of the energy produced by the original CO_2 formation to drive the chemical steps of the process assuming no losses. However, the actual energy requirements for steps 1 and 2 could be much more considerable.

Thermodynamics II - pressure of CO_2: Best estimate (Lackner *et. al* 1998) of working pressure is 6 bar, although higher pressure will speed the reaction. Carbonation will proceed at 1 bar CO_2 but will be slower. Relatively few data for the kinetics exist however. Indications are that this will be the rate determining step, and that the hydroxide formation from the silicate will be quicker.

Kinetics: Best estimate suggests that $Mg(OH)_2$ can be completely carbonated in 1 hour by CO_2 at 20 bar. i.e. residence time in the carbonation reaction should be 1 hour.

Other chemicals: An estimate of 1000 t HCl will be required for the initial priming of the plant which will be continuously recycled. Concentrated (20 moles per litre) HCl has been assumed (Lackner *et. al.* 1998), therefore using 1.4×10^6 litres. Note that if less concentrated HCl is used, it will require the estimate for the amount of energy required for H_2O evaporation to be revised upwards.

Bi-products: Primary bi-products will be SiO_2, Fe, Ni, Mn and Cr

Estimated CO_2 take-up: Best estimate for the reaction is approximately 80% take-up.

CO_2 output: Potential CO_2 savings are critically dependent on the thermal re-circulation capacity of the plant.

B. Cost:

Mine capital: The sequestration process assumes that the feed material is either a serpentine or peridotite. At this stage of process selection the feed rock is assumed to have a multiplier of 3 when compared to the amount of CO_2 safely sequestered and accordingly a 9 Mtpy open pit has been costed. An open pit of this size will have an approximate capital cost of US$25 M based on a number of varying parameters. The mine will operate for 312 days per annum for a total daily production of 28,800 t delivered to the crushing and screening plant.

Mine operating: The variable mining cost for a 28,800 tpd mine will be in the region of US$1.25/t. This cost includes all drill, blast and load, haul, dump operations for an open pit operation.

Plant capital: The cost of the stockpile area, crushing and grinding plant for a 1,000 t/hr operation is estimated at $50M, based on operation for 350 days per year. The chemical plant for the sequestration process has been costed at $540M and involves multiple reaction vessels for the acid dissolution and carbonation process, thickeners, multiple-effect falling film evaporators, and rotary vacuum filters.

Plant operating: Operating cost of the comminution circuit has been estimated at $1.68/t based on a power cost of $0.05/kWhr. Operating costs for the chemical plant have been estimated at $14/t.

Clean-up:

- Quarry: can work out whole area, restore for recreation, potentially use low cost backfill of carbonate/silica material, although working difficulties, double handling cost, water contamination problems, etc.
- Tailings/storage area: options include large lagoon (say 4 km^2 x 25 m depth minimum) which will require ongoing monitoring and final restoration. Low toxicity except silica dust.
- Process plant: low toxicity processes except dusts and CO_2 leaks. Minimal plant contamination and therefore relatively low decommissioning costs (c.f. nuclear plant,

plastics manufacture etc.). Low toxicity of processes equals proportionately low cost clean-up, although surface workings will be extensive.

C. Confidence:

Scale-up factor: Compatible with modern chemical process technology.

Complexity of plant: Low-moderate.

Novelty of process: New process, but utilises known technology.

D. Acceptance:

Mine safety: There are no known hazards associated with the proposed mining method that cannot be safely dealt with in existing legislation and by implementing internationally accepted good engineering practice. All mining operations have potential areas of concern but the mining of these magnesium-rich silicate rocks can be likened to the extraction of building aggregates, which is a process undertaken in almost every developed and third world nation, and which have good proven safe working practices.

Plant safety: No particular safety issues associated with the plant other than those covered by government Health and Safety Policy.

Chemical hazards:

- CO_2 leakage: possible asphixiant.
- If allowed to dry, SiO_2 dust from tailings (<10 micron) can be classed as respirable dust and therefore present problems of irritation and risk of silicosis respiratory illness. Similarly, carbonate dust can also be classed as respirable dust and thus a lung irritant, but is not believed directly toxic.
- Explosives storage/accidents, etc.

Environmental issues:

- Land take/use high – quarry, plant and tailings.
- Hydrology effects with respect to quarrying and waste disposal.
- Visual impact high – plant, quarry and tailings.
- Noise, dust, blasting, CO_2 leakage.
- Metal content, form, stability in the final product.
- Disposal method and final soil stability.

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

E. Applicability:

Availability of and location of source material: For this method to proceed, a plentiful source of magnesium silicate rock is required such as serpentinite, peridotite or dunite. In nature, these rocks are relatively common and can be found on all the world's continents. In addition, many regions of the world where fossil fuel power generation is prevalent have ready, local sources of these rock types. Good examples are east and west USA, much of northern Europe and many parts of Japan.

Demand needs: Plentiful raw materials throughout world, therefore wide choice of sites. Uses standard technology or derivatives – no novel technology.

Capacity of technology: A combination of modern mining, mineral processing and chemical processing methods should easily meet the technology requirement for this type of plant. For target of 1 Gt CO_2/yr by 2025, would need more than 300 such plants if this were the only option. Production facilities to meet equipment demand for this scale should not be a limiting factor.

Verdict:

Method 1 relies on the use of a relatively common feedstock (ultramafic rocks), utilises standard technology for the process, and does not present any unassailable environmental problems. Conversely, the cost of the plant and infrastructure is high whilst the overall CO_2 saving may be minimal due to the high energy usage of the evaporation stage of the reaction. However, all things considered, this method represents an approach which can be thoroughly investigated to a relatively high degree of accuracy to provide a marker for other potential mineral carbonate based sequestration methods.

5.2.2 Method 2

A. Efficiency of reaction:

Description: Extract pure, saturated $MgCl_{2(aq)}$ from naturally occurring brine, convert to powdered hydroxide, react with CO_2, dispose of $MgCO_3$ and $HCl_{(aq)}$ products. This, in effect, is a modification of Method 1. Figure 5.4 illustrates the main reaction stages and hourly tonnages, whilst Figure 5.5 presents the summary information for the process.

Equations:

Dehydration

$$MgCl_{2(aq)} + H_2O_{(l)} \xrightarrow{-H_2O\text{ of solution}} Mg(OH)Cl_{(s)} + HCl_{(g)}$$

Repartitioning of Mg(OH)Cl

$$2Mg(OH)Cl_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + MgCl_{2(aq)}$$

Figure 5.4: Flowsheet for Method 2 (tonnages per hour)

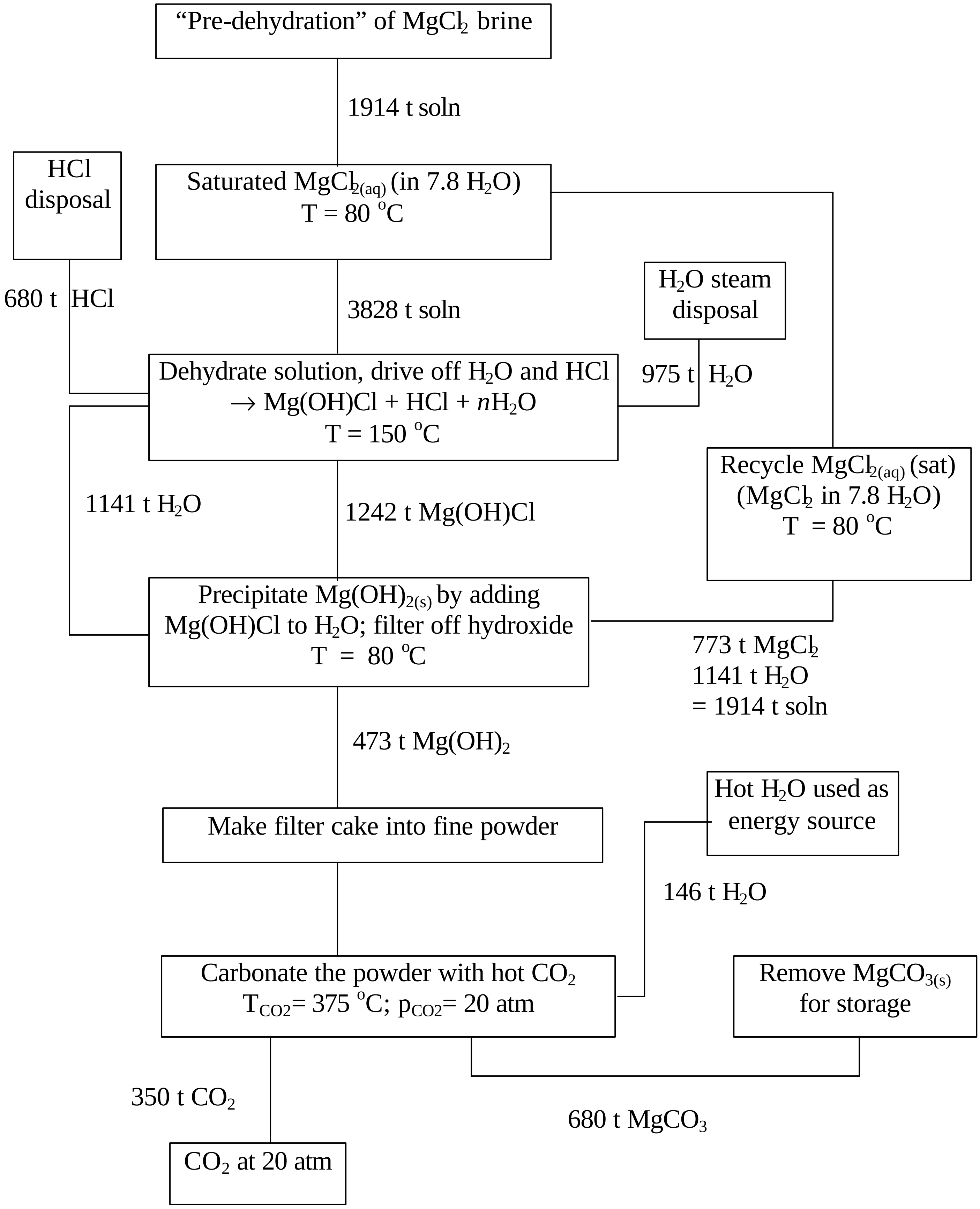
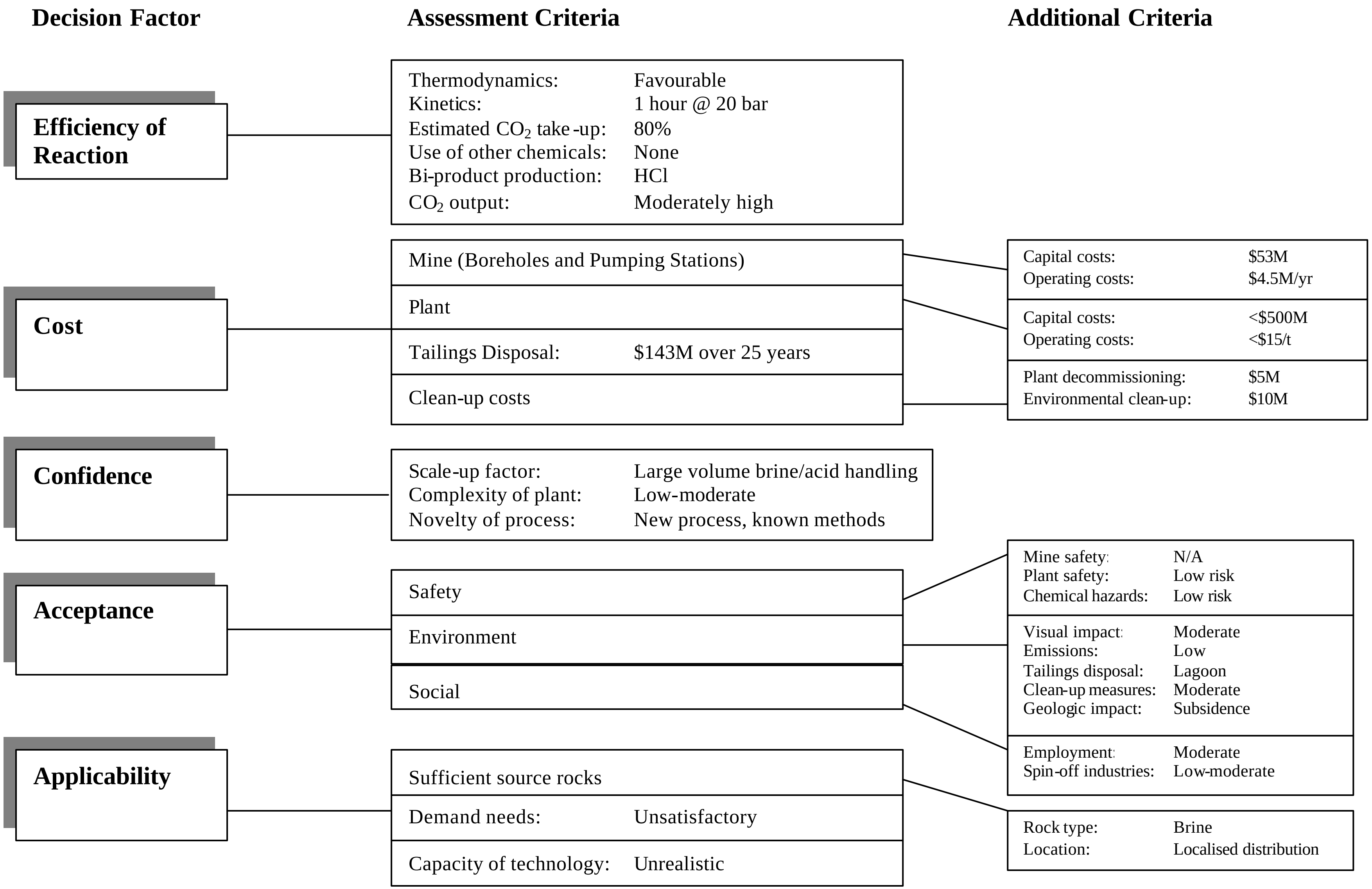


Figure 5.5: Method 2 – Use of Magnesium Chloride-rich Brine



Decision Factor | **Assessment Criteria** | **Additional Criteria**

Efficiency of Reaction

Thermodynamics: Favourable
Kinetics: 1 hour @ 20 bar
Estimated CO_2 take-up: 80%
Use of other chemicals: None
Bi-product production: HCl
CO_2 output: Moderately high

Cost

Mine (Boreholes and Pumping Stations)
- Capital costs: $53M
- Operating costs: $4.5M/yr

Plant
- Capital costs: <$500M
- Operating costs: <$15/t

Tailings Disposal: $143M over 25 years

Clean-up costs
- Plant decommissioning: $5M
- Environmental clean-up: $10M

Confidence

Scale-up factor: Large volume brine/acid handling
Complexity of plant: Low-moderate
Novelty of process: New process, known methods

Acceptance

Safety
- Mine safety: N/A
- Plant safety: Low risk
- Chemical hazards: Low risk

Environment
- Visual impact: Moderate
- Emissions: Low
- Tailings disposal: Lagoon
- Clean-up measures: Moderate
- Geologic impact: Subsidence

Social
- Employment: Moderate
- Spin-off industries: Low-moderate

Applicability

Sufficient source rocks
- Rock type: Brine
- Location: Localised distribution

Demand needs: Unsatisfactory
Capacity of technology: Unrealistic

Carbonation

$$Mg(OH)_{2(aq)} + CO_{2(g)} \xrightarrow{CO_2\ 20\ bar} MgCO_{3(s)} + H_2O_{(g)}$$

Mass flow: Liquid starting material, solid and liquid products. Table 5.2 below shows the sequestering potential of $MgCl_2$ brine.

Table 5.2: Sequestering Potential of Brine

Starting material	**Mass of $MgCl_2$ (t) required to store 1t CO_2**	Mass of product (t) for each 1t of CO_2			Mass of product (t) for each 1t of brine		
		$MgCO_3$/t	HCl/t	**Total/t**	$MgCO_3$/t	HCl/t	**Total/t**
$MgCl_2$	**2.2**	1.9	1.7	**3.6**	0.9	0.8	**1.7**

If a saturated $MgCl_2$ solution can be assumed, then the process would require 4,000 litres per tonne of CO_2

Thermodynamics I - heat flow: Need to consider the energy flows for the processes per tonne of CO_2 sequestered (= 2.3×10^4 moles).

i. Extraction of $Mg(OH)_2$:
Process is similar to the production starting from the silicate, but this time the HCl and H_2O from the $MgCl_{2(aq)}$ must both be removed. Net energy requirement for all steps prior to carbonation (Lackner *et. al.* 1998) is 9.6×10^6 kJ per tonne CO_2, which assumes that none of the energy of the evaporated H_2O and HCl can be harnessed.

ii. Carbonation of $Mg(OH)_2$ at 375 °C:

Energy released:	9.1×10^5 kJ per tonne CO_2
Energy required to reach reaction temp:	7.9×10^5 kJ per tonne CO_2

Since one can only gain 8.9×10^6 kJ per tonne CO_2 formed, then in the worst case this method requires more CO_2 than it sequesters. In the best case, one should be able to derive heat from recondensing the evaporated H_2O and HCl and if all this potential were harnessed then only 20% of the amount of CO_2 sequestered would be required (as an output from energy production) for the process to run.

As in Method 1, it is the dehydration step to produce $Mg(OH)_2$ which will most likely be the crucial step in determining whether the process is viable.

Thermodynamics II - pressure of CO_2: Best estimate (Lackner *et. al* 1998) of working pressure is 6 bar, although higher pressure will speed the reaction. Carbonation will proceed at 1 bar CO_2 but will be slower. Relatively few data for the kinetics exist however. Indications are that this will be the rate determining step, and that the hydroxide formation from the silicate will be quicker.

Kinetics: Best estimate suggests that $Mg(OH)_2$ can be completely carbonated in 1 hour by CO_2 at 20 bar. i.e. residence time in the carbonation reaction should be 1 hour.

Other chemicals: No other chemicals are required in this process, although HCl will be produced in prodigious quantities.

Bi-products: None, assuming the original brine is pure.

Estimated CO_2 take-up: Best estimate for the reaction is approximately 80% take-up.

CO_2 output: Potential CO_2 savings are critically dependent on the thermal re-circulation capacity of the plant, as like method 1, the dehydration stage is likely to be the most energy intensive.

B. Cost:

Mine capital: The model is based on a brine requirement of 1.4 Ml/hr to feed the sequestration plant. Data from CSMA experience is based on the costs from Geothermal Research and indicates that for a 2,200m borehole a pressure drop of 10 Mpa can be reasonably expected at the wellhead for a 24 l/sec flow rate of brine produced.

Pumps operating at 80% efficiency will provide some 70,000 l/hr giving a total estimated number of pumps and production wells as 20. Much of the borehole and pump information comes from Harrison *et al* (1990).

Two capital costs apply:

Borehole Installation: The base case is assumed to be a 8.5" cased hole to a depth of say 2,200m. Typical costs for drilling and completing such a hole is estimated at US$1 M per 1,000m or US$2.2M per completed hole. In comparison, personal communication indicates a local Canadian cost of US$700,000 per hole. Total capital requirement is US$44 M.

Pump Installation: Capital cost is based on the formula:

$c_s=(495+/-9)W_p+(110+/-30)D_s+(17,600+/-2,000)$

where

c_s= cost of purchasing and installing a downhole poduction well pump and associated equipment (US $ 1988 terms)
Wp= hydraulic power required in the production well (kW)
Ds= production pump setting depth (m)

The power requirement is defined as Pressure Drop (Pa)x Flow rate (l/sec) which gives, in this model, a need for some 240 kW per pump.

Substituting the figures into the equation gives a range of prices between $309k and $450k. An average figure of say US $380k has been assumed and inflated using the US PPI (producer price index 1988-1998) to US$445k per pump installation. Total capital for 20 installations is approximately US $9 M.

Mine operating: Two costs apply for the operation of the system:

Pump Energy Cost: The pump efficiencies are assumed to be 80% and the fractional load factor (time in use) is assumed at 98%. The unit price of electricity is US$0.05/kWh.

The calculated yearly energy cost is US $2.6M for all production pumps.

Pump Maintenance Costs: The annual maintenance cost is based on the number of pumps and the original capital cost of installation.

The estimated annual cost of maintenance is US $1.9M

Plant capital: It is not possible to provide a capital cost for the plant, although it will be comparable in cost to the plant proposed for Method 1, although without the comminution circuit, the plant should be marginally cheaper.

Plant operating: Operating costs for the chemical plant have been estimated at approximately $14/t.

Clean-up:

- Absence of quarry would require storage area for waste products.
- Tailings/storage area: options include large lagoon (say 4 km^2 x 25 m depth minimum) which will require ongoing monitoring and final restoration. Low toxicity.
- Acid disposal: huge volume of produced acid will present a major problem, re-injection is the only feasible disposal route. Deep injection disposal of hazardous and industrial waste does occur, on a smaller scale than required here, but in this instance is probably environmentally unacceptable.

C. Confidence:

Scale-up factor: The process should scale-up for large industrial usage, although large volumes of brine/acid will present handling difficulties.

Complexity of plant: Low-moderate.

Novelty of process: New process, but utilising known methods.

D. Acceptance:

Mine safety: Not applicable, pumping stations only.

Plant safety: No particular safety issues associated with the plant, other than the handling of large quantities of acid. Other measures covered by government Health and Safety Policy.

Chemical hazards:
- CO_2 leakage: possible asphixiant.
- Carbonate dust: <10 micron is classed as respirable dust (lung irritant, but not believed directly toxic).
- HCl in process plant and for disposal.

Environmental issues:
- Land take/use lower than Method 1, with widely spread pumping stations feeding a central plant and tailings facility.
- Subsidence from brine extraction (12 million m^3 required to sequester 3Mt CO_2).
- Acid generation/disposal. 3Mt CO_2 will produce 5.1 Mt HCl
- Hydrology/groundwater effects re carbonate and acid disposal.
- Visual impact different to Method 1.
- Noise, CO_2 leakage, acid containment and disposal.
- Metal content, form, stability in the final product – this will depend on the composition of the brine.

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

E. Applicability:

Availability and location of source material: This method requires Mg-rich brine as the feedstock, which in nature is found, not exclusively, associated with large continental evaporitic basins. Such basins can be found in Canada, USA, Brazil, parts of Europe and other areas of the world. However, only a small proportion of evaporite basins contain sufficient brine to support large scale sequestration, and also, those that do, rarely have enough geologic information to allow prediction of suitable brine reservoirs.

Demand needs: Brine aquifers are probably not sufficiently extensive, have enough capacity or porosity/conductivity to permit high output, and therefore long term pumping. As an example of the volumes of brine required, to satisfy the sequestration demand of 3 Mt CO_2/yr would require the processing of 1,370,000 litres/hour of brine.

Capacity of technology: Pumping/drilling technology could be derived from the oil/gas industry. Multiple pumping stations could supply a potential flow of 1.5 Ml/hr, but high volume evaporation technology may prove difficult.

Verdict:

The use of magnesium-rich brine in the sequestration process has been rejected for a number of reasons:

- Naturally occurring brines of suitable chemistry are rare in nature;
- The large volumes of brine required for the process, if taken from evaporite sequences, are likely to cause severe surface subsidence, and
- The process generates huge volumes of HCl which must be disposed of either at surface or returned underground. Neither option is environmentally acceptable.

5.2.3 Method 3a

Methods 1 and 2 involve substantial H_2O evaporation. In an effort to reduce this somewhat it has been proposed (Wendt *et. al.* 1998b) that a $MgCl_2.nH_2O$ ($n = 3.5$) melt may be used as a solvent either for the synthesis of $Mg(OH)_2$ or for direct carbonation of silicate rock (Method 3b).

A. Efficiency of reaction:

Description: Mine and crush Mg silicate rock (for the purposes of the simplified flowsheet, a pure serpentine feed is assumed), dissolve in molten hydrated $MgCl_2$ (which is recycled), react with CO_2, dispose of $MgCO_3$, SiO_2 and bi-products. Figure 5.6 illustrates the main reaction stages, whilst Figure 5.7 presents the summary information for the process.

Equations:

Activate the serpentinite so that it will dissolve readily in hydrated $MgCl_2$ melt.

$$\tfrac{1}{3}Mg_3Si_2O_5(OH)_{4(s)} + MgCl_{2(l)} + H_2O_{(l)} \longrightarrow 2Mg(OH)Cl_{(s)} + \tfrac{2}{3}SiO_{2(s)}$$

Dilution of this will precipitate out $Mg(OH)_2$ for the carbonation step.

$$2Mg(OH)Cl_{(s)} \xrightarrow{H_2O} MgCl_{2(aq)} + Mg(OH)_{(s)}$$

At this stage the SiO_2 and $Mg(OH)_2$ are separated from the solution and used in the carbonation

$$Mg(OH)_{2(s)} + CO_{2(g)} \longrightarrow MgCO_{3(s)} + H_2O_{(g)}$$

Meanwhile the $MgCl_2$ is partially dehydrated to regenerate $MgCl_2.3.5H_2O$ for the melt.

$$MgCl_{2(aq)} \xrightarrow{-4.3H_2O} MgCl_2.3.5H_2O_{(l)}$$

Figure 5.6: Flowsheet for Method 3a (tonnages per hour)

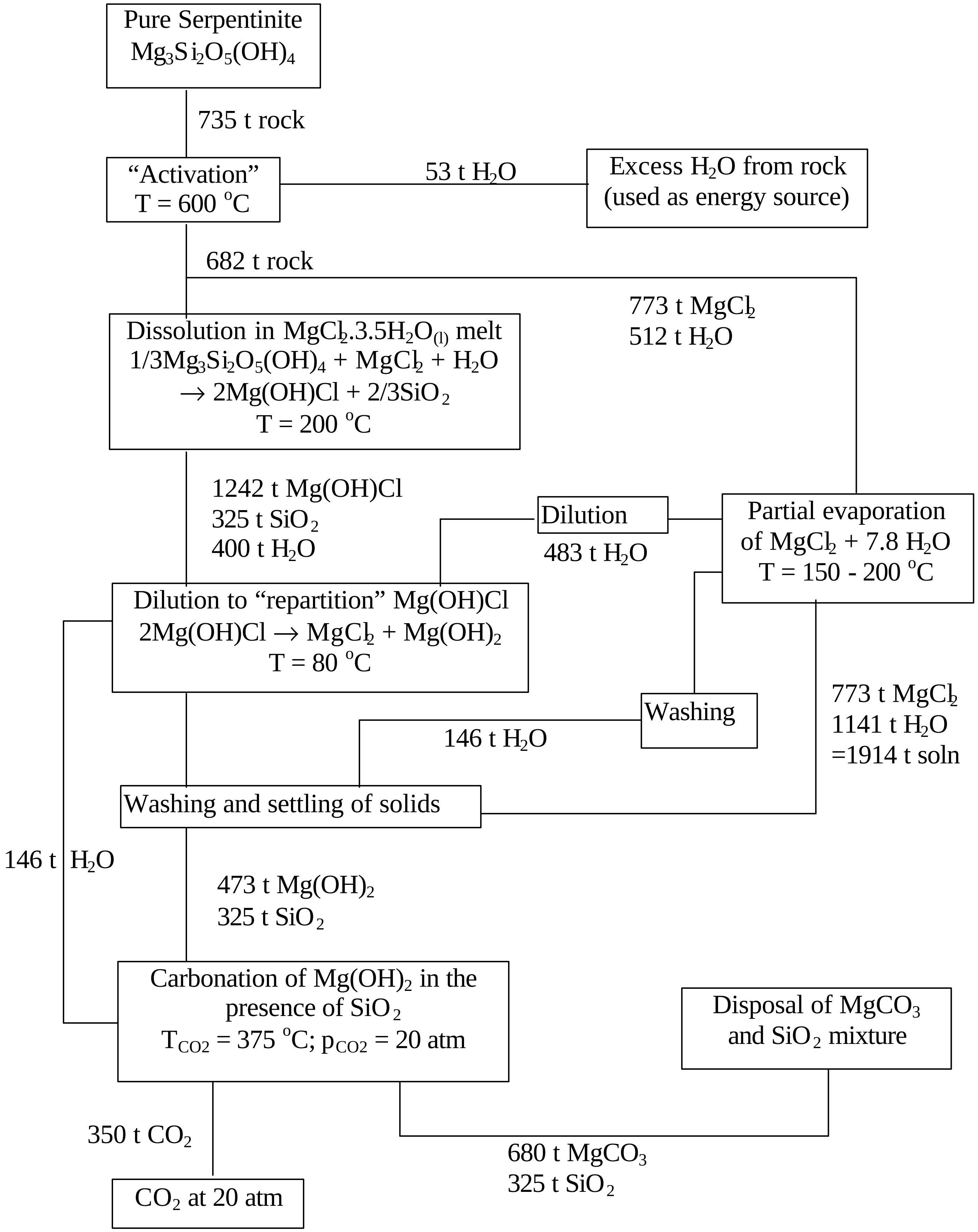
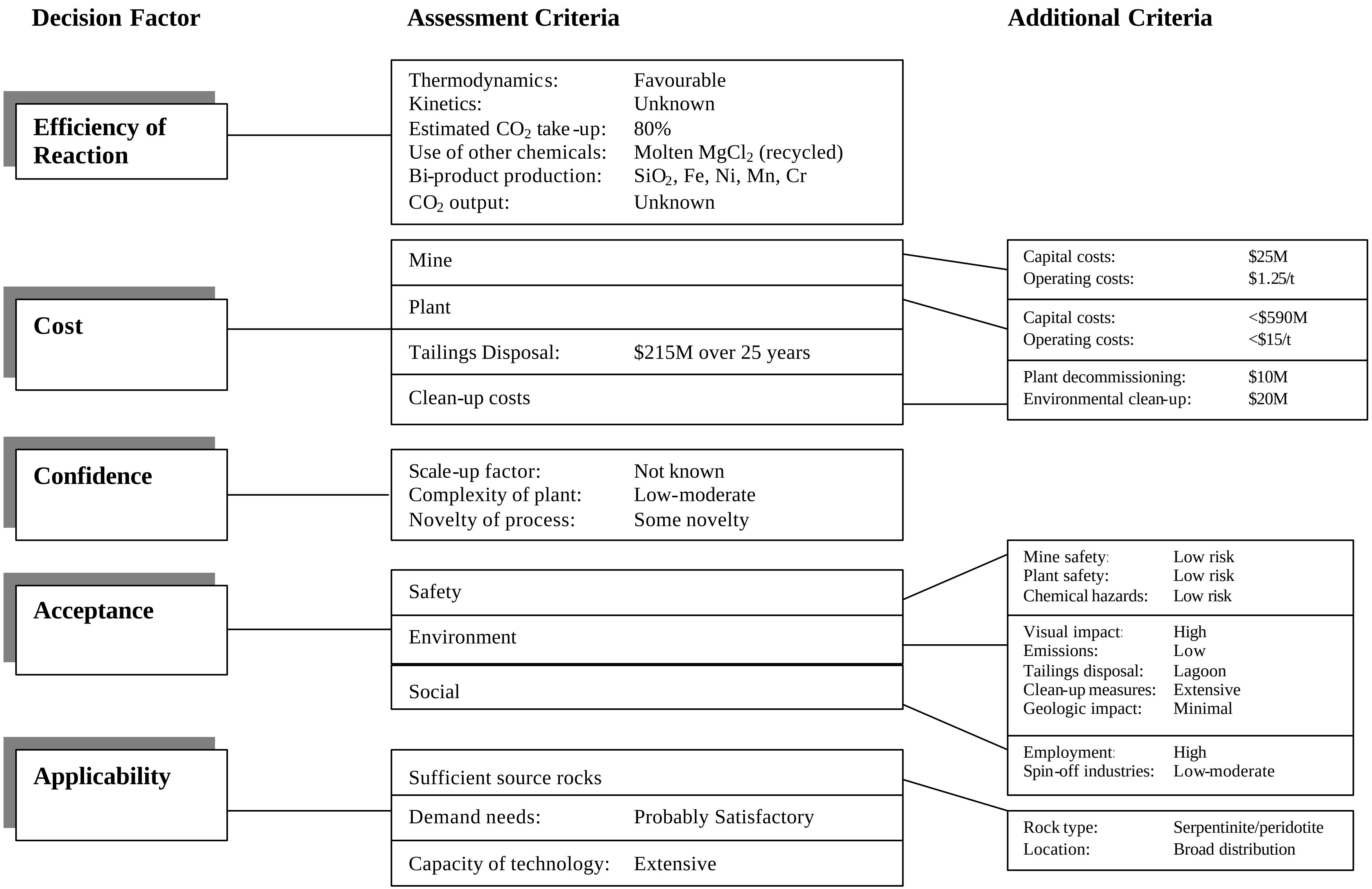


Figure 5.7: Method 3a – Dissolution of Magnesium Silicate-rich Rock in Molten $MgCl_2$



Decision Factor | **Assessment Criteria** | **Additional Criteria**

Efficiency of Reaction

Thermodynamics:	Favourable
Kinetics:	Unknown
Estimated CO_2 take-up:	80%
Use of other chemicals:	Molten $MgCl_2$ (recycled)
Bi-product production:	SiO_2, Fe, Ni, Mn, Cr
CO_2 output:	Unknown

Cost

Mine
- Capital costs: $25M
- Operating costs: $1.25/t

Plant
- Capital costs: <$590M
- Operating costs: <$15/t

Tailings Disposal: $215M over 25 years

Clean-up costs
- Plant decommissioning: $10M
- Environmental clean-up: $20M

Confidence

Scale-up factor:	Not known
Complexity of plant:	Low-moderate
Novelty of process:	Some novelty

Acceptance

Safety
- Mine safety: Low risk
- Plant safety: Low risk
- Chemical hazards: Low risk

Environment
- Visual impact: High
- Emissions: Low
- Tailings disposal: Lagoon
- Clean-up measures: Extensive
- Geologic impact: Minimal

Social
- Employment: High
- Spin-off industries: Low-moderate

Applicability

Sufficient source rocks
- Rock type: Serpentinite/peridotite
- Location: Broad distribution

Demand needs: Probably Satisfactory

Capacity of technology: Extensive

This method requires about half the amount of evaporation of H_2O as Method 1 and furthermore since the melt rather than HCl is used to dissolve the rock, there is no requirement to generate HCl (which costs energy).

Mass flow: Solid starting materials and solid/slurry products only (same as for Method 1). Table 5.3 shows the sequestering potential of some pure minerals.

Table 5.3: Sequestering Potential of some Pure Minerals

Starting rock	**Mass of rock (t) required to store 1t CO_2**	Mass of product (t) for each 1t of CO_2			Mass of product (t) for each 1t of silicate rock		
		$MgCO_3$/t	SiO_2/t	**Total/t**	$MgCO_3$/t	SiO_2/t	**Total/t**
Forsterite Mg_2SiO_4	**1.6**	1.9	0.7	**2.6**	1.2	0.43	**1.63**
Serpentine $Mg_3Si_2O_5(OH)_4$	**2.1**	1.9	0.9	**2.8**	0.91	0.43	**1.34**
Olivine $MgSiO_3$	**2.3**	1.9	1.4	**3.3**	0.84	0.60	**1.64**

Thermodynamics I - heat flow: Best estimate (Wendt *et. al.* 1998c) is that the overall energy consumption will correspond to producing about 40% of the amount of CO_2 which is sequestered, i.e. 3.6×10^6 kJ per tonne of CO_2 sequestered.

Thermodynamics II - pressure of CO_2: Best estimate (Wendt *et. al* 1998c) of working pressure is 10-20 bar. Carbonation will not proceed at 1 bar in this case. Also note that a preheating of the serpentine will also be required to 600 ^{o}C and this will be a major heat requirement.

Kinetics: It is not known whether this route is kinetically viable because no studies have been performed.

Other chemicals: Molten hydrated $MgCl_2$ will be required. An estimate of 1200 t will be required in the plant which will be continuously recycled, but this number may have to be revised because the reaction kinetics will determine the scale of reaction.

Bi-products: Primary bi-products will be SiO_2, Fe, Ni, Mn and Cr.

Estimated CO_2 take-up: Best estimate for the reaction is approximately 80% take-up.

CO_2 output: Unknown, as the kinetics of the reaction are uncertain.

B. Cost:

Mine capital: The sequestration process assumes that the feed material is either a serpentine or peridotite. At this stage of process selection the feed rock is assumed to have multiplier of

3 when compared to the amount of CO_2 safely sequestered and accordingly a 9 Mtpy open pit has been costed. An open pit of this size will have an approximate capital cost of US$25 M based on a number of varying parameters. The capital cost equates to some US$871 per daily tonne of material. The mine will operate for 312 days per annum for a total daily production of 28,800 t delivered to the crushing and screening plant.

Mine operating: The variable mining cost for a 28,800 tpd mine will be in the region of US$1.25/t. This cost includes all drill, blast and load, haul, dump operations for an open pit operation.

Plant capital: The cost of the stockpile area, crushing and grinding plant for a 1,000 t/hr operation is estimated at $50M, based on operation for 350 days per year. It is not possible to estimate the cost of the plant as the kinetics are unknown. However, if the kinetics were favourable, it is likely that the plant would be less expensive than that proposed for Method 1.

Plant operating: Operating cost of the comminution circuit has been estimated at $1.68/t based on a power cost of $0.05/kWhr. Operating costs are likely to be less than estimated for Method 1.

Clean-up:

- Quarry: can work out whole area, restore for recreation, potentially use low cost backfill of carbonate/silica material, although working difficulties, double handling cost, water contamination problems, etc.
- Tailings/storage area: options include large lagoon (say 4 km^2 x 25 m depth minimum) which will require ongoing monitoring and final restoration. Low toxicity except silica dust.
- Process plant: low toxicity processes except dusts and CO_2 leaks. Minimal plant contamination and therefore relatively low decommissioning costs (c.f. nuclear plant, plastics manufacture etc.). Low toxicity of processes equals proportionately low cost clean-up, although surface workings will be extensive.

C. Confidence:

Scale-up factor: Not known, but probably feasible.

Complexity of plant: Low-moderate.

Novelty of process: Some novelty, as the kinetics of various aspects of the reactions are unknown.

D. Acceptance:

Mine safety: There are no known hazards associated with the proposed mining method that cannot be safely dealt with in existing legislation and by implementing internationally accepted good engineering practice. All mining operations have potential areas of concern but the mining of these magnesium-rich silicate rocks can be likened to the extraction of building aggregates, which is a process undertaken in almost every developed and third world nation, and which have good proven safe working practices.

Plant safety: No particular safety issues associated with the plant other than those covered by government Health and Safety Policy.

Chemical hazards:
- CO_2 leakage: asphixiant – associated with pipeline and processing plant.
- If allowed to dry, SiO_2 dust from tailings (<10 micron) can be classed as respirable dust and therefore present problems of irritation and risk of silicosis respiratory illness. Similarly, carbonate dust can also be classed as respirable dust and thus a lung irritant, but is not believed directly toxic.
- Explosives storage/accidents, etc.

Environmental issues:
- Land take/use high – quarry, plant and tailings.
- Hydrology effects with respect to quarrying and waste disposal.
- Visual impact high – plant (may be smaller than Method 1), quarry and tailings.
- Noise, dust, blasting, CO_2 leakage.
- Metal content, form, stability in the final product.
- Disposal method and final soil stability.

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

E. Applicability:

Availability of and location of source material: For this method to proceed, a plentiful source of magnesium silicate rock is required such as serpentinite, peridotite or dunite. In nature, these rocks are relatively common and can be found on all the world's continents. In addition, many regions of the world where fossil fuel power generation is prevalent have ready, local sources of these rock types. Good examples are east and west USA, much of northern Europe and many parts of Japan.

Demand needs: Plentiful raw materials throughout world, therefore wide choice of sites. Can be expected to use standard technology or derivatives – no novel technology – but the process engineering will depend upon reaction kinetics.

Capacity of technology: A combination of modern mining, mineral processing and chemical processing methods should easily meet the technology requirement for this type of plant. For target of 1 Gt CO_2/yr by 2025, would need more than 300 such plants if this were the only option. Production facilities to meet equipment demand for this scale should not be a limiting factor.

Verdict:

Method 3a has the major disadvantage that the reaction kinetics are unknown. However, should the process be feasible over a suitable time frame, it still suffers from two serious energy consuming steps:

- Partial dehydration of the feed (elevate temperature to 600°C) before dissolution, and
- Evaporation stage.
- It is likely that both of these steps will combine to render the net CO_2 savings of the process negligible.

5.2.4 Method 3b

Efficiency of reaction:

Description: This route has been proposed (Wendt *et. al.* 1998b) in order to reduce the evaporation requirements of Methods 1, 2, and 3a. Mine and crush Mg silicate rock (for the purposes of the simplified flowsheet, a pure serpentine feed is assumed), dissolve in molten hydrated $MgCl_2$ (which is recycled), react directly with high pressure CO_2 in the melt, dispose of $MgCO_3$ and SiO_2 products. Figure 5.8 illustrates the main reaction stages and hourly tonnages, whilst Figure 5.9 presents the summary information for the process.

Equations:

React the serpentinite with CO_2 (at > 30bar) in molten hydrated $MgCl_2.nH_2O$ ($n = 3.5$)

$$\tfrac{1}{3}Mg_3Si_2O_5(OH)_{4(s)} + CO_{2(g)} \xrightarrow{MgCl_2.3.5H_2O} MgCO_{3(s)} + \tfrac{2}{3}SiO_{2(s)} + \tfrac{2}{3}H_2O_{(l)}$$

Then the $MgCO_3$ and SiO_2 solids are separated from the melt (it is not clear how) and the excess H_2O (which comes from the rock) is removed and the melt is recycled. Effectively HCl is produced in a catalytic amount, so this is effectively a one-pot version of Method 1.

The thermodynamics of this process have been shown to be favourable (Wendt *et. al.* 1998b); but the kinetics are not understood (if the reaction is very slow then it will not be viable on the desired scale). Energy is required to maintain the temperature of the melt and evaporate off a small amount of H_2O (originally from the rock), but these inputs should be relatively small.

Mass flow: solid starting materials and products only (same as for Methods 1 and 3a above). Table 5.4 shows the sequestering potential of some pure minerals.

Figure 5.8: Flowsheet for Method 3b (tonnages per hour)

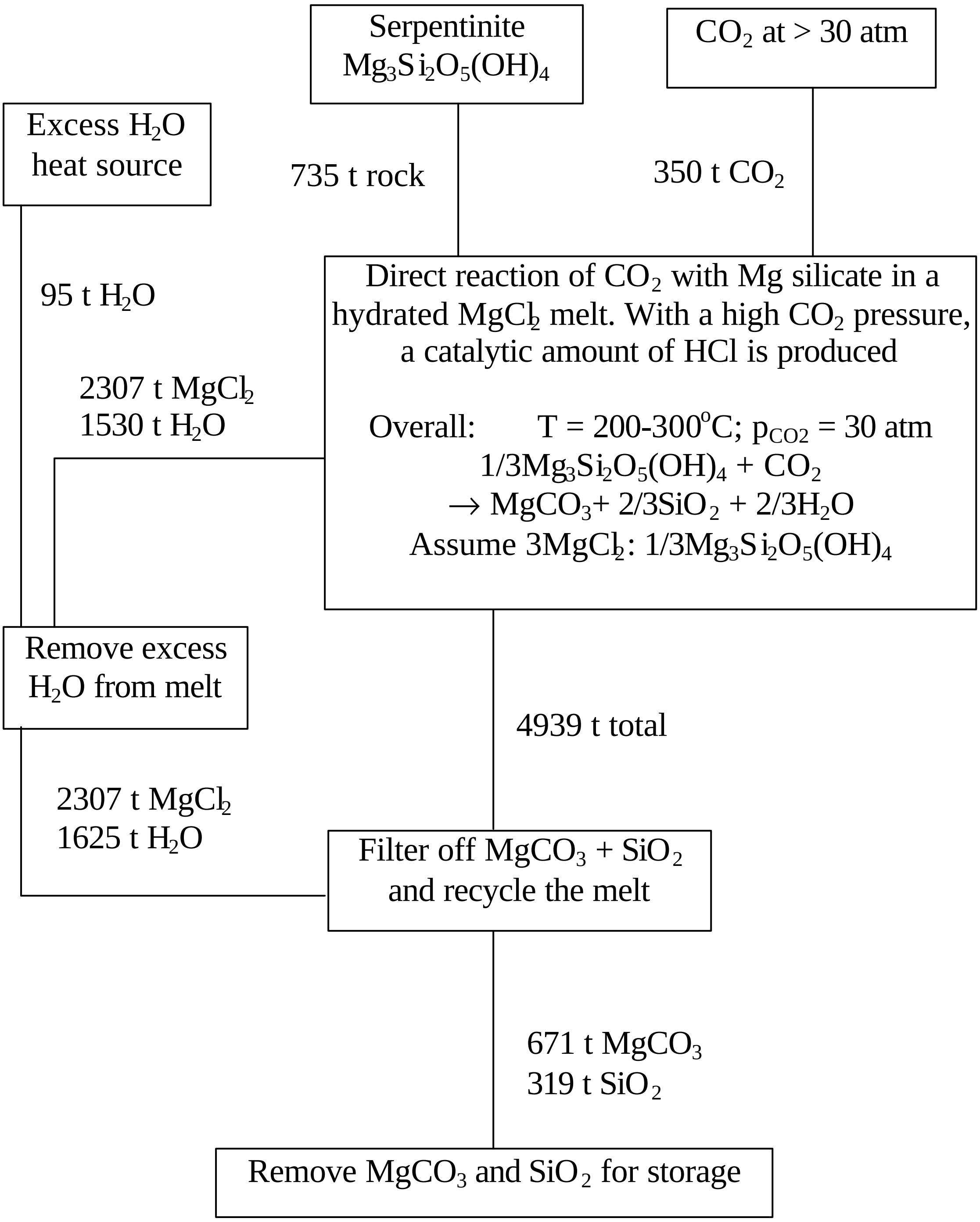
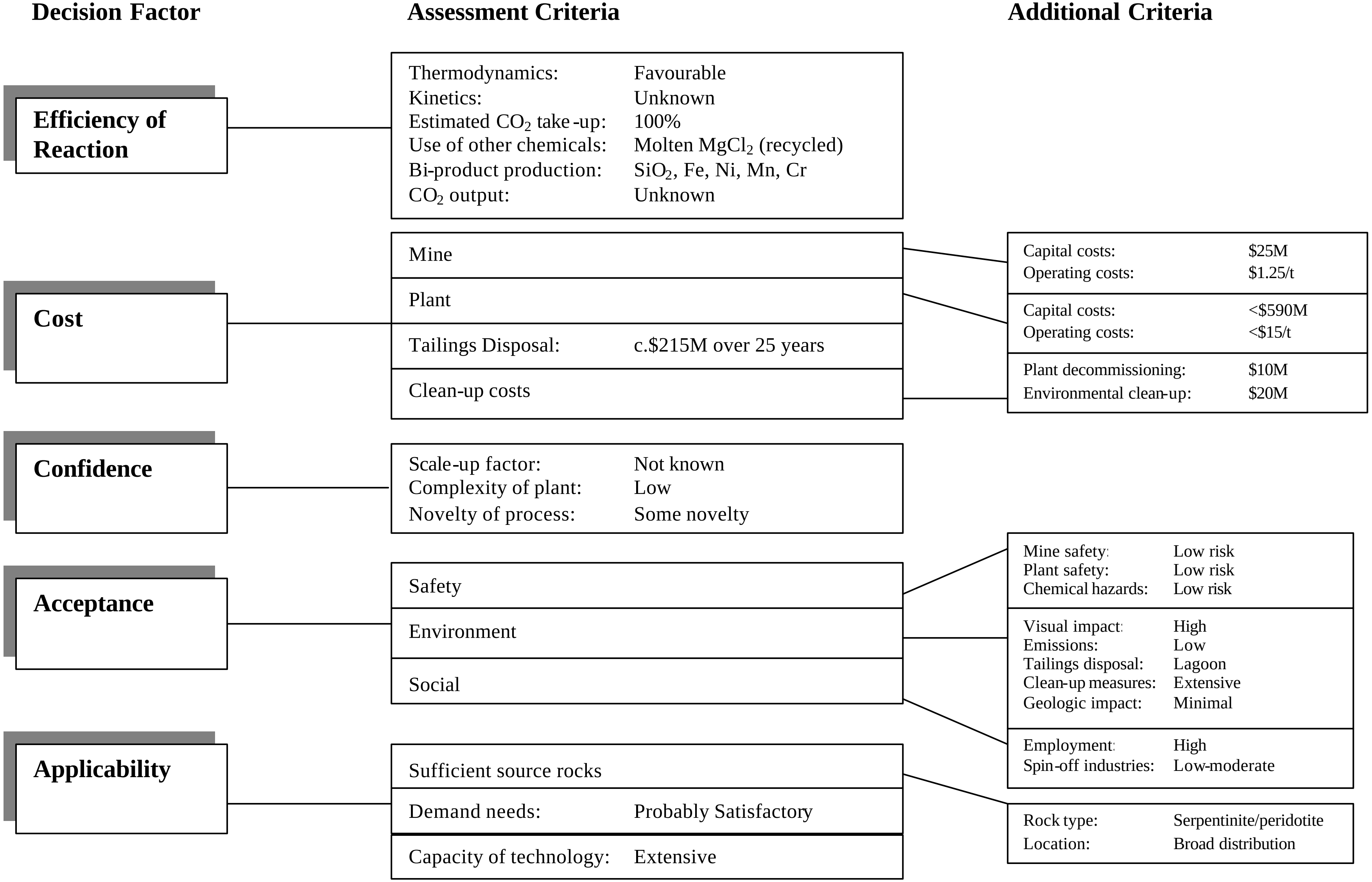


Figure 5.9: Method 3b – Direct Carbonation in Molten $MgCl_2$



Decision Factor

Assessment Criteria

Additional Criteria

Efficiency of Reaction

Thermodynamics: Favourable
Kinetics: Unknown
Estimated CO_2 take-up: 100%
Use of other chemicals: Molten $MgCl_2$ (recycled)
Bi-product production: SiO_2, Fe, Ni, Mn, Cr
CO_2 output: Unknown

Cost

Mine
- Capital costs: $25M
- Operating costs: $1.25/t

Plant
- Capital costs: <$590M
- Operating costs: <$15/t

Tailings Disposal: c.$215M over 25 years

Clean-up costs
- Plant decommissioning: $10M
- Environmental clean-up: $20M

Confidence

Scale-up factor: Not known
Complexity of plant: Low
Novelty of process: Some novelty

Acceptance

Safety
- Mine safety: Low risk
- Plant safety: Low risk
- Chemical hazards: Low risk

Environment
- Visual impact: High
- Emissions: Low
- Tailings disposal: Lagoon
- Clean-up measures: Extensive
- Geologic impact: Minimal

Social
- Employment: High
- Spin-off industries: Low-moderate

Applicability

Sufficient source rocks
- Rock type: Serpentinite/peridotite
- Location: Broad distribution

Demand needs: Probably Satisfactory

Capacity of technology: Extensive

Table 5.4: Sequestering Potential of some Pure Minerals

Starting rock	**Mass of rock (t) required to store 1t CO_2**	Mass of product (t) for each 1t of CO_2			Mass of product (t) for each 1t of silicate rock		
		$MgCO_3$/t	SiO_2/t	**Total/t**	$MgCO_3$/t	SiO_2/t	**Total/t**
Forsterite Mg_2SiO_4	**1.6**	1.9	0.7	**2.6**	1.2	0.43	**1.63**
Serpentine $Mg_3Si_2O_5(OH)_4$	**2.1**	1.9	0.9	**2.8**	0.91	0.43	**1.34**
Olivine $MgSiO_3$	**2.3**	1.9	1.4	**3.3**	0.84	0.60	**1.64**

Thermodynamics I – heat flow: Steam from evaporation can in principal be used to maintain the temperature of the melt. The overall reaction of CO_2 with the rock is exothermic and as this is taking place in the melt (rather than in a separate gas-solid reaction as in methods 1,2, and 3a) this energy will be available. However estimates (Wendt *et. al.* 1998b) suggest that some external heat will still be required.

Thermodynamics II – pressure of CO_2: Carbonation of must be carried out at about 30 bar.

Kinetics: It is not known whether this route is kinetically viable because no studies have been performed.

Other chemicals: The other major chemical will be molten hydrated $MgCl_2$. Estimate will be for 3800 tonnes required in the plant assuming a ratio of Mg in the chloride to Mg in the silicate of 3:1. This will be continuously recycled.

Bi-products: Primary bi-products will be SiO_2, Fe, Ni, Mn and Cr.

Estimated CO_2 take-up: It is possible that this process route will sequester 100% of the provided CO_2.

CO_2 output: Not known, no kinetic data, although if the process can run to completion in a short time, then the process has the potential for low CO_2 output in terms of energy consumed.

Cost:

Mine capital: The sequestration process assumes that the feed material is either a serpentine or peridotite. At this stage of process selection the feed rock is assumed to have multiplier of 3 when compared to the amount of CO_2 safely sequestered and accordingly a 9 Mtpy open pit has been costed. An open pit of this size will have an approximate capital cost of US$25 M based on a number of varying parameters. The capital cost equates to some US$871 per daily tonne of material. The mine will operate for 312 days per annum for a total daily production of 28,800 t delivered to the crushing and screening plant.

Mine operating: The variable mining cost for a 28,800 tpd mine will be in the region of US$1.25/t. This cost includes all drill, blast and load, haul, dump operations for an open pit operation.

Plant capital: The cost of the stockpile area, crushing and grinding plant for a 1,000 t/hr operation is estimated at $50M, based on operation for 350 days per year. It is not possible to estimate the cost of the plant as the kinetics are unknown. However, if the kinetics were favourable, it is likely that the plant would be less expensive than that proposed for Method 1.

Plant operating: Operating cost of the comminution circuit has been estimated at $1.68/t based on a power cost of $0.05/kWhr. Operating costs are likely to be less than estimated for Method 1.

Clean-up:

- Quarry: can work out whole area, restore for recreation, potentially use low cost backfill of carbonate/silica material, although working difficulties, double handling cost, water contamination problems, etc.
- Tailings/storage area: options include large lagoon (say 4 km^2 x 25 m depth minimum) which will require ongoing monitoring and final restoration. Low toxicity except silica dust.
- Process plant: low toxicity processes except dusts and CO_2 leaks. Minimal plant contamination and therefore relatively low decommissioning costs (c.f. nuclear plant, plastics manufacture etc.). Low toxicity of processes equals proportionately low cost clean-up, although surface workings will be extensive.

C. Confidence:

Scale-up factor: Not known, but probably feasible.

Complexity of plant: Low.

Novelty of process: Some novelty, as the kinetics of various aspects of the reactions are unknown.

D. Acceptance:

Mine safety: There are no known hazards associated with the proposed mining method that cannot be safely dealt with in existing legislation and by implementing internationally accepted good engineering practice. All mining operations have potential areas of concern but the mining of these magnesium-rich silicate rocks can be likened to the extraction of building aggregates, which is a process undertaken in almost every developed and third world nation, and which have good proven safe working practices.

Plant safety: No particular safety issues associated with the plant other than those covered by government Health and Safety Policy.

Chemical hazards:

- CO_2 leakage: asphixiant – associated with pipeline and processing plant.
- If allowed to dry, SiO_2 dust from tailings (<10 micron) can be classed as respirable dust and therefore present problems of irritation and risk of silicosis respiratory illness. Similarly, carbonate dust can also be classed as respirable dust and thus a lung irritant, but is not believed directly toxic.
- Explosives storage/accidents, etc.

Environmental issues:

- Land take/use high – quarry, plant and tailings.
- Hydrology effects with respect to quarrying and waste disposal.
- Visual impact high – plant (may be smaller than Method 3a), quarry and tailings.
- Noise, dust, blasting, CO_2 leakage.
- Metal content, form, stability in the final product.
- Disposal method and final soil stability.

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

E. Applicability:

Availability of and location of source material: For this method to proceed, a plentiful source of magnesium silicate rock is required such as serpentinite, peridotite or dunite. In nature, these rocks are relatively common and can be found on all the world's continents. In addition, many regions of the world where fossil fuel power generation is prevalent have ready, local sources of these rock types. Good examples are east and west USA, much of northern Europe and many parts of Japan.

Demand needs: Plentiful raw materials throughout world, therefore wide choice of sites. Can be expected to use standard technology or derivatives – no novel technology – but the process engineering will depend upon reaction kinetics.

Capacity of technology: A combination of modern mining, mineral processing and chemical processing methods should easily meet the technology requirement for this type of plant. For target of 1 Gt CO_2/yr by 2025, would need more than 300 such plants if this were the only option. Production facilities to meet equipment demand for this scale should not be a limiting factor.

Verdict:

Although the kinetics are unknown for this method, if the process can be demonstrated to work on a realistic timeframe, then this method offers the best opportunity to sequester CO_2 at reasonable cost and high efficiency.

5.2.5 Method 4

A. Efficiency of reaction:

Description: Mine and crush Ca silicate rock, dissolve in HCl, convert to powdered hydroxide, dissolve in H_2O, react with CO_2, dispose of $CaCO_3$ and SiO_2 products. Figure 5.10 illustrates the main reaction stages and hourly tonnages, whilst Figure 5.11 presents the summary information for the process.

Overall equation: $CaCO_{3(s)} + 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)} \xrightarrow{eqm} CaCl_{2(aq)} + 2NaHCO_{3(s)}$

Sequestration equation: $Ca(OH)_{2(aq)} + CO_{2(g)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)}$

Mass flow: Solid starting materials and products only. Table 5.5 details the sequestering properties of a $CaSiO_3$ feed.

Table 5.5: Sequestering Properties of a $CaSiO_3$ Feed

Starting rock	**Mass of rock (t) required to store 1t CO_2**	Mass of product (t) for each 1t of CO_2			Mass of product (t) for each 1t of silicate rock		
		$CaCO_3$/t	SiO_2/t	**Total/t**	$CaCO_3$/t	SiO_2/t	**Total/t**
$CaSiO_3$	**2.7**	2.3	1.4	**3.7**	0.86	0.52	**1.38**

The above mass flow assumes pure Ca silicate rock, but in reality, it is probably not possible to obtain this. In addition, calcium sources are much more dilute than Mg sources. Therefore, these numbers will most likely need to be increased by a factor of about 5. This is a major problem with this route.

Thermodynamics I - heat flow:

i. Extraction of $Ca(OH)_2$:
The extraction of $Ca(OH)_2$ from the silicate requires some Mg(OH)Cl to be cycled through the process (Lackner *et.al.* 1998). The overall extraction procedure is quite similar to that used to extract $Mg(OH)_2$ from the silicate, but has not been given so much attention. Since an extra step is required it is probably reasonable to assume that the energy input will be about 20-40% of the amount derived from forming CO_2, although there will be further complications if the source rock is not pure.

ii. Carbonation of $Ca(OH)_2$ at room temp:
The carbonation is in principle quite exothermic, but since the hydroxide is so dilute, there will be nothing more than a gentle heating of the water.

Figure 5.10: Flowsheet for Method 4 (tonnages per hour)

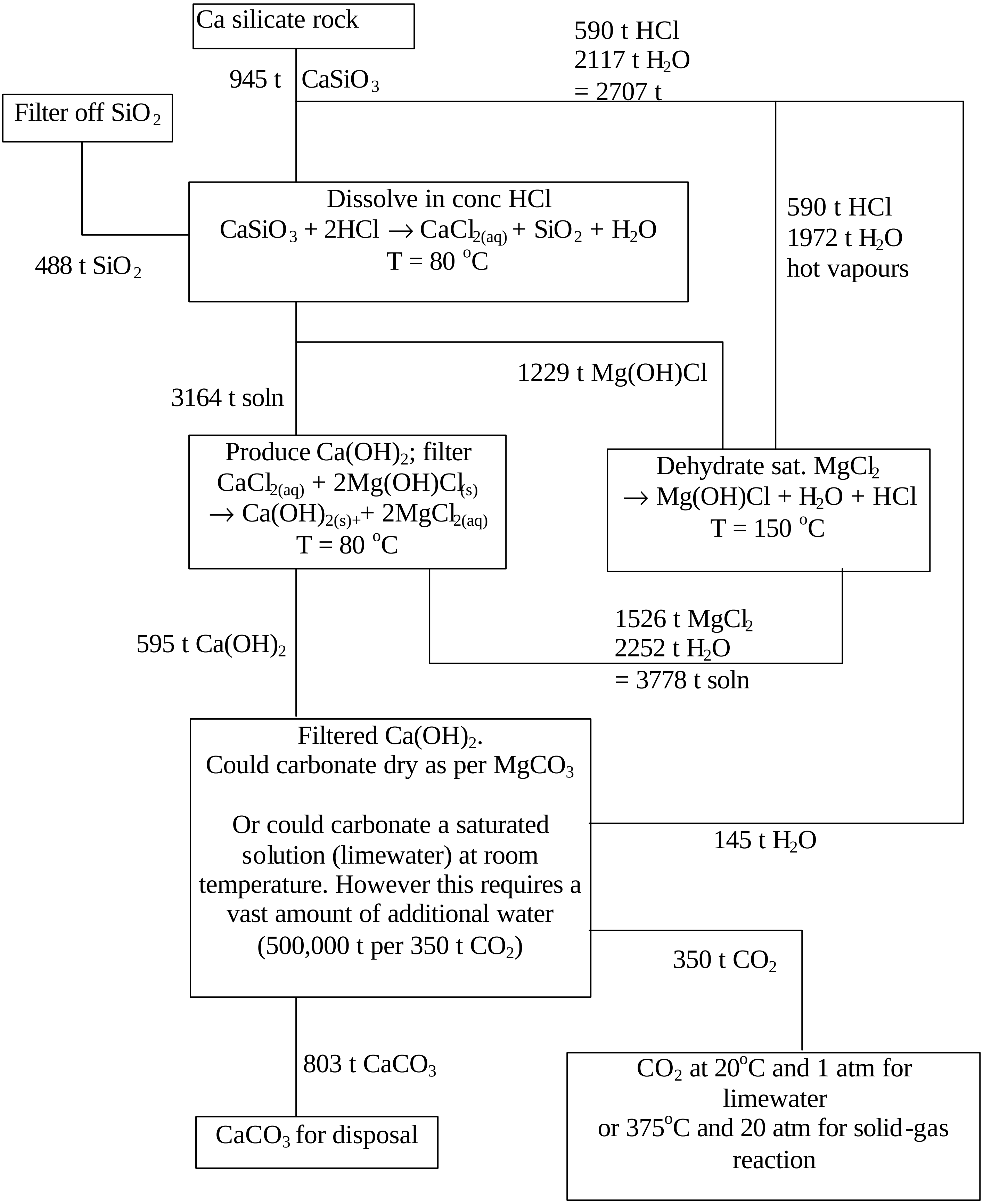
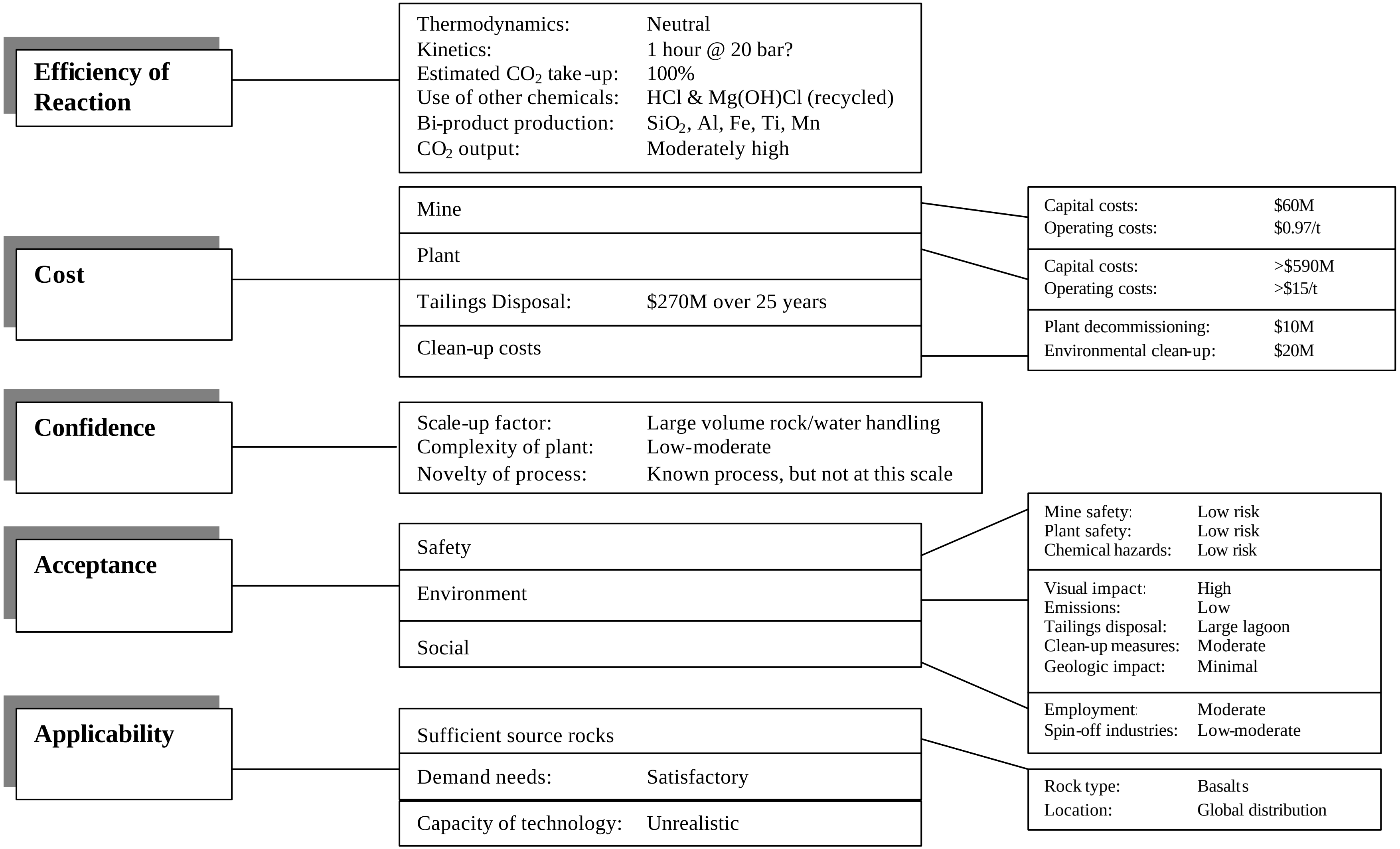


Figure 5.11: Method 4 – Dissolution of calcium Silicate-rich Rock



Decision Factor | **Assessment Criteria** | **Additional Criteria**

Efficiency of Reaction

Thermodynamics: Neutral
Kinetics: 1 hour @ 20 bar?
Estimated CO_2 take-up: 100%
Use of other chemicals: HCl & Mg(OH)Cl (recycled)
Bi-product production: SiO_2, Al, Fe, Ti, Mn
CO_2 output: Moderately high

Cost

Mine
- Capital costs: $60M
- Operating costs: $0.97/t

Plant
- Capital costs: >$590M
- Operating costs: >$15/t

Tailings Disposal: $270M over 25 years

Clean-up costs
- Plant decommissioning: $10M
- Environmental clean-up: $20M

Confidence

Scale-up factor: Large volume rock/water handling
Complexity of plant: Low-moderate
Novelty of process: Known process, but not at this scale

Acceptance

Safety
- Mine safety: Low risk
- Plant safety: Low risk
- Chemical hazards: Low risk

Environment
- Visual impact: High
- Emissions: Low
- Tailings disposal: Large lagoon
- Clean-up measures: Moderate
- Geologic impact: Minimal

Social
- Employment: Moderate
- Spin-off industries: Low-moderate

Applicability

Sufficient source rocks
- Rock type: Basalts
- Location: Global distribution

Demand needs: Satisfactory
Capacity of technology: Unrealistic

Thermodynamics II - pressure of CO_2: 1bar of CO_2 is required. The gas is bubbled through the solution of the hydroxide.

Kinetics: The kinetics here are fast. On a small scale this route is used for the precipitation of pure $CaCO_3$ (but derived originally from the carbonate)

Other chemicals: Other chemicals will be HCl and Mg(OH)Cl. Estimate will be for 1000 tonnes required in the plant which will be continuously recycled. Concentrated (20 moles per litre) HCl has been assumed for the Mg process (Lackner *et. al.* 1998) so the volume is 1.4×10^6 litres of conc. HCl.

Bi-products: This process would produce SiO_2, large quantities of Al and Fe, and lesser amounts of Ti and Mn.

Estimated CO_2 take-up: Potentially 100% as the CO_2 can be repeatedly bubbled through the limewater solution.

CO_2 output: This method is to be energy intensive as the dehydration stage will require considerable heat energy input.

B. Cost:

Mine capital: This method requires the mining of basalts for the calcium silicate content. The source rock multiplier in this instance would be approximately 9:1 against CO_2 sequestered. An open pit of some 28 Mtpy is indicated with an estimated capital cost of US$60 M.

Mine operating: The variable mining cost will be in the region of US$0.97/t delivered to the crushing and screening plant.

Plant capital: The cost of the comminution plant based on a throughput of approximately 3,000 t/hr has been estimated at $95M, based on operation for 350 days per year. The cost of the chemical plant could well be more expensive than that proposed for Method 1 due to the very large volumes of material being processed.

Plant operating: There is little economy of scale achieved at these levels of production, giving an estimated comminution plant operating cost of $1.68/t. The operating cost of the chemical plant is likely to be in excess of $15/t.

Clean-up:
- Quarry: can work out whole area, restore for recreation, potentially use low cost backfill of carbonate/silica material, although working difficulties, double handling cost, water contamination problems, etc.
- Tailings/storage area: very large lagoon area will require ongoing monitoring, no restoration before 25 years, possibility of backfill to quarry, or use several small lagoons. Low toxicity except silica dust, although high levels of aluminium and iron.

- Process plant: low toxicity processes except dusts and CO_2 leaks. Minimal plant contamination – low decommissioning costs (c.f. nuclear plant, plastics manufacture etc.).
- Process water reservoir, filtration lagoons – low cost depending on size. Low toxicity of processes equals proportionately low cost clean-up, but workings will be extensive.

C. Confidence:

Scale-up factor: Reaction equipment should scale-up to industrial plant, although very large quantities of silicate feedstock and prodigious volumes of water need to be accommodated.

Complexity of plant: Low-moderate.

Novelty of process: Process is well known, but not on a large industrial scale.

D. Acceptance:

Mine safety: There are no known hazards associated with the proposed mining method that cannot be safely dealt with in existing legislation and by implementing internationally accepted good engineering practice. All mining operations have potential areas of concern but the mining of these basalts can be likened to the extraction of building aggregates, which is a process undertaken in almost every developed and third world nation, and which have good proven safe working practices.

Plant safety: No particular safety issues associated with the plant other than those covered by government Health and Safety Policy.

Chemical hazards:

- CO_2 leakage: asphixiant – associated with pipeline and processing plant.
- If allowed to dry, SiO_2 dust from tailings (<10 micron) can be classed as respirable dust and therefore present problems of irritation and risk of silicosis respiratory illness. Similarly, carbonate dust can also be classed as respirable dust and thus a lung irritant, but is not believed directly toxic.
- Explosives storage/accidents, etc.

Environmental issues:

- Land take/use very high – quarry, plant and tailings.
- Hydrology effects re quarrying and waste disposal.
- Visual impact high – plant (may be smaller than Method 1), but quarry and tailings will be vast.
- Noise, dust, blasting, CO_2 leakage.
- High water requirement for hydration of $Ca(OH)_2$.
- High levels of metals produced.
- Disposal – extraction of $CaCO_3$ from huge volumes of carbonated limewater – 0.5 M m^3/hr $CaCO_3$ solution = 342 t/hr CO_2

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

E. Applicability:

Availability and location of source material: The feedstock for a reaction using CaO would most likely be basaltic material which occurs naturally in abundant quantities, far more so than the potential magnesium feeds detailed above. Basalts can be found globally, and as a potential reserve of CaO, can be considered to be unlimited. The principal drawback to this source of CaO is that the CaO content of typical basalts rarely exceeds 13% by weight (c.f. MgO in serpentinites of approximately 35%).

Demand needs: Plentiful raw materials (basalts) throughout world, therefore wide choice of sites. Generally uses standard technology or derivatives, but requires a high efficiency 'molecular filter' to concentrate $CaCO_3$ from the reacted limewater.

Capacity of technology: The $Ca(OH)_2$ will be as an aqueous solution, therefore large volumes of fluid will need to be reacted which produces a suspension of colloidal $CaCO_3$. Need approx. 1450 t of $Ca(OH)_2$ solution (1,450,000 litres) per tonne of CO_2 sequestered. The carbonate would not settle out and disposal to surface water is unacceptable so would need:

- a 'molecular filter' to strain off the $CaCO_3$ for storage and water recycling;
- the ability to evaporate water from the end product cheaply and replace the process water, and
- filter and recharge approximately 10,000 t of reacted limewater every 1.2 minutes if the water was recycled to meet the annual 3Mt/y CO_2 target.

Apart from the volumes of solutions required/produced the main technology constraints concern extracting the 'solid' $CaCO_3$ from the aqueous solution of reacted 'limewater'. A combination of modern mining, mineral processing and chemical processing methods should meet the other technology requirement for this type of plant.

Verdict:

This approach of using calcium silicate feed as the sequestering medium has been rejected for a number of reasons:

- Extremely large volumes of water are required for the hydration of $Ca(OH)_2$ – estimates of 0.5 Mt per hour have been made;
- Due to the high volumes of fluid required, tailings lagoons would be vast, and
- Inability to practically filter and recharge huge volumes of limewater to meet CO_2 demands.

5.2.6 Method 5

Efficiency of Reaction:

Description: Dissolve $MgCO_3$ from dolomite in seawater. React this with CO_2 at 10 atm to produce $MgCl_2$ in solution and $NaHCO_3$ in solution. Precipitate 87% of the latter by adding a large amount of NaCl from a store (either mined or obtained from a massive desalination process). Remove the solid $NaHCO_3$ and the $CaCO_3$ (undissolved component of the dolomite). Then run the reaction in reverse on the remaining 13%, recycle the CO_2 and recycle most of the NaCl in the NaCl/$MgCl_2$ solution by evaporation. Dispose of the excess NaCl and $MgCl_2$ to the sea. Store the solids in the ground or at sea. Figure 5.12 illustrates the main reaction stages and hourly tonnages, whilst Figure 5.13 presents the summary information for the process.

Equations:

$$MgCO_{3(s)} + 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)} \xrightarrow{eqm} MgCl_{2(aq)} + 2NaHCO_{3(s)}$$

Note that The $CaCO_3$ present in dolomite will be removed as a solid.

Mass flow: Solid starting materials and products only. An example of a mass balance for a pure $MgCO_3$ feed are given in Table 5.6.

Table 5.6: Sequestering Properties of a Pure $MgCO_3$ Feed

Starting materials		**Mass of rock (t) required to store 1t CO_2**	Mass of product (t) for each 1t CO_2			Mass of product (t) for each 1t of starting rock.		
$MgCO_3$	NaCl		$MgCl_2$/t	$NaHCO_3$/t	**Total/t**	$MgCl_2$/t	$NaHCO_3$/t	**Total/t**
1.9	2.7	**4.6**	2.2	3.8	**6.0**	0.47	0.84	**1.3**

The actual mass of carbonate rock required (dolomite) will depend on the proportion of $MgCO_3$ and $CaCO_3$ within the feed.

Thermodynamics I – heat flow: The reactions run at room temperature. The evaporation of NaCl is not necessary for the success of the process providing a sufficiently large store of NaCl is available - this could be obtained by an enormous evaporation operation or by mining an evaporite deposit.

Thermodynamics II - pressure of CO_2: 10 bar of CO_2 is required to drive the reaction in favour of the products.

Kinetics: The timescale seems to be relatively fast - approximately 1 hour residence time in the reaction chamber including the time taken up adding the NaCl slurry.

Figure 5.12: Flowsheet for Method 5 (tonnages per hour)

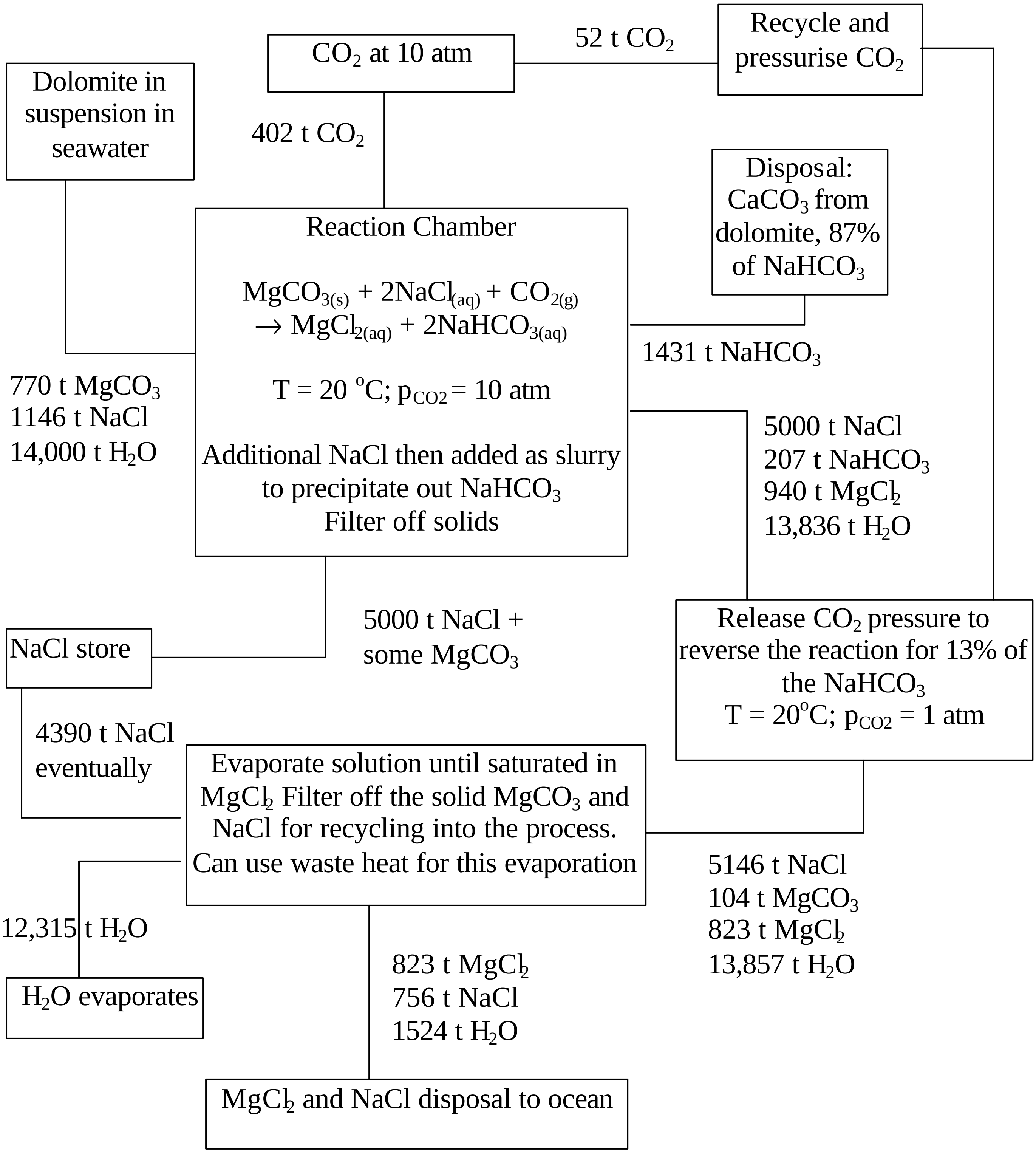
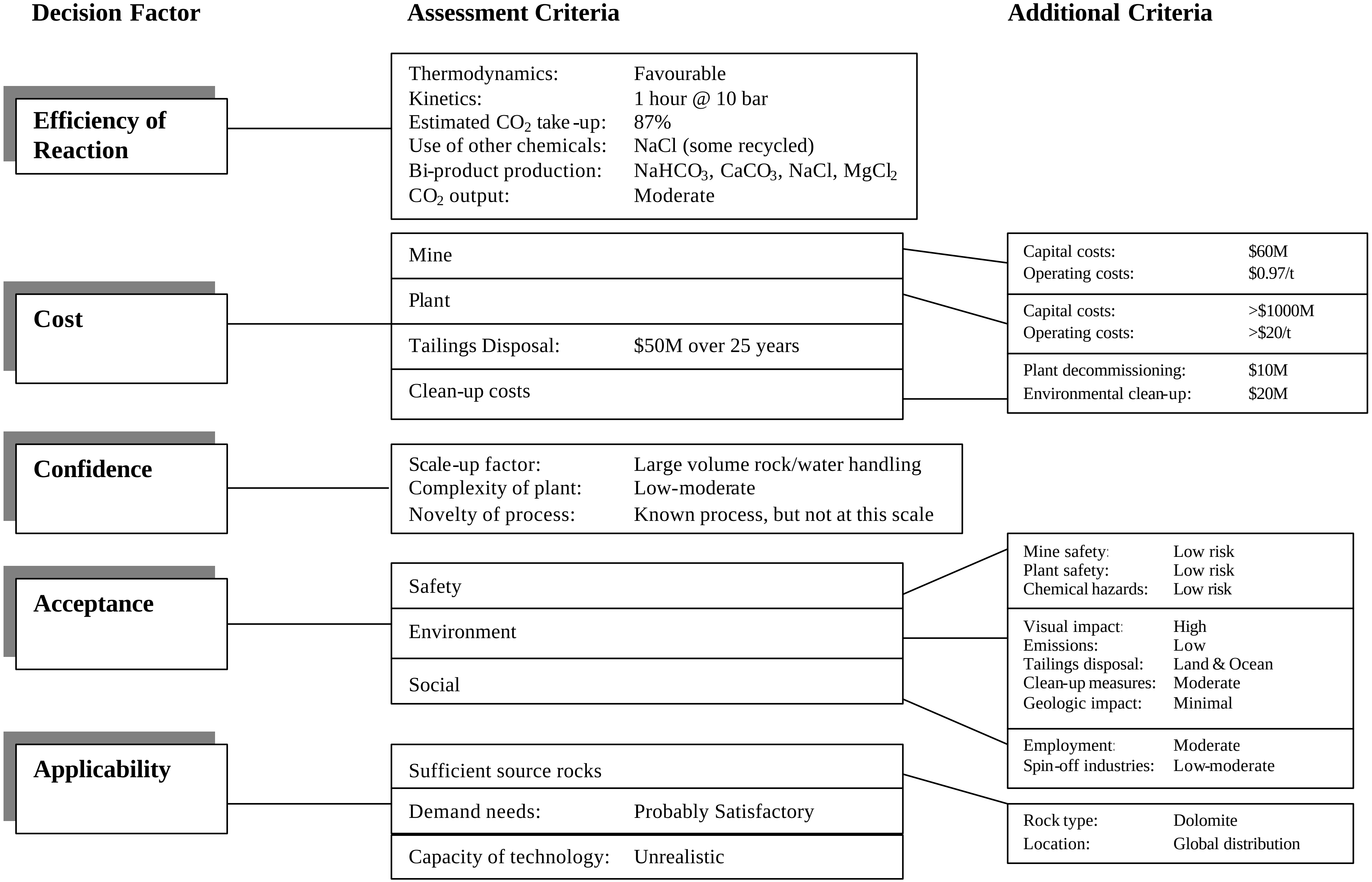


Figure 5.13: Method 5 – Dissolution of calcium Silicate-rich Rock



Decision Factor | **Assessment Criteria** | **Additional Criteria**

Efficiency of Reaction

- Thermodynamics: Favourable
- Kinetics: 1 hour @ 10 bar
- Estimated CO_2 take-up: 87%
- Use of other chemicals: NaCl (some recycled)
- Bi-product production: $NaHCO_3$, $CaCO_3$, NaCl, $MgCl_2$
- CO_2 output: Moderate

Cost

- Mine
  - Capital costs: $60M
  - Operating costs: $0.97/t
- Plant
  - Capital costs: >$1000M
  - Operating costs: >$20/t
- Tailings Disposal: $50M over 25 years
- Clean-up costs
  - Plant decommissioning: $10M
  - Environmental clean-up: $20M

Confidence

- Scale-up factor: Large volume rock/water handling
- Complexity of plant: Low-moderate
- Novelty of process: Known process, but not at this scale

Acceptance

- Safety
  - Mine safety: Low risk
  - Plant safety: Low risk
  - Chemical hazards: Low risk
- Environment
  - Visual impact: High
  - Emissions: Low
  - Tailings disposal: Land & Ocean
  - Clean-up measures: Moderate
  - Geologic impact: Minimal
- Social
  - Employment: Moderate
  - Spin-off industries: Low-moderate

Applicability

- Sufficient source rocks
  - Rock type: Dolomite
  - Location: Global distribution
- Demand needs: Probably Satisfactory
- Capacity of technology: Unrealistic

Other chemicals: The process uses very large amounts of seawater, but this should present few problems. $NaHCO_3$ could in principle be stored dry, however, it is fairly soluble and will eventually find its way to the sea where it will tend to raise the pH and may release some CO_2 back to the atmosphere.

Bi-products: Primary bi-products will be $CaCO_3$ and $NaHCO_3$ solids and aqueous NaCl and $MgCl_2$.

Estimated CO_2 take-up: The potential for the process is to sequester 100%, although the various reactions only allow for an 87% take-up – the remainder is either recycled or returned to the atmosphere.

CO_2 output: Potentially, this process could have relatively low CO_2 outputs if a plant can be designed to meet the requirements of the reactions and throughputs.

Cost:

Mine capital: The sequestration process assumes that the feed material is a dolomite rock with variable composition. To meet the demands of 350 t CO_2 per hour would require approximately 1700 t per day of dolomite rock, i.e., approximately a 5:1 ratio. This tonnage requirement commands a capital cost of US$30 M based on a number of varying parameters. The mine will operate for 312 days per year for a total daily production of 40,800 t delivered to the crushing and screening plant.

Mine operating: The variable mining cost for a 40,800 tpd mine will be in the region of US$1.15/t. The cost includes all drill, blast and load, haul, dump operations for an open pit mine.

Plant capital: Due to serious concerns as to the viability of the plant with regard to the enormous volumes of liquids to be moved around and filtered, an estimate for the capital cost of the plant has been put at > US$1 billion. This cost also excludes any additional expenditure required for the procurement of NaCl.

Plant operating: Operating costs for a plant of the magnitude considered are expected to be in excess of US$20 per tonne.

Clean-up: Clean-up costs will be higher than some other methods due to the size of the quarry, need for seawater pumping and reservoir facilities, salt storage, the size of the processing plant and evaporation facilities.

Confidence:

Scale-up factor: Conceptually possible to design a plant to handle the large tonnages of solids and volumes of liquids required by the process.

Complexity of plant: Low-moderate.

Novelty of process: Established process, but not tried at this scale.

Acceptance:

Mine safety: There are no known hazards associated with the proposed mining method that cannot be safely dealt with in existing legislation and by implementing internationally accepted good engineering practice. All mining operations have potential areas of concern but the mining of these magnesium-rich silicate rocks can be likened to the extraction of building aggregates, which is a process undertaken in almost every developed and third world nation, and which have good proven safe working practices.

Plant safety: No particular safety issues associated with the plant other than those covered by government Health and Safety Policy.

Chemical hazards:
- CO_2 leakage, asphixiant, associated with the pipeline and processing plant.
- Calcium carbonate dust: <10 micron is classed as respirable (lung irritant but not believed directly toxic).

Environmental issues:
- Major issue regarding alteration of ocean chemistry through disposal of $NaHCO_3$ and $MgCl_2$ process products to the sea.
- High landtake compared with Methods 1 and 3.
- Hydrological issues – dolomites may be significant aquifers.
- Visual impact – high re. quarry, tailings dam, evaporation lagoons, pumping/storage facilities and coastal location.
- Noise, dust, blasting, CO_2 leakage.
- Ground stability of land sites used for $NaHCO_3$ disposal.

Social issues: Increased local employment, secondary employment, infrastructure improvements, but agriculture land loss, enforced resettlement, soil erosion, water contamination. Wide range of pros and cons depending on the site and regional economy.

Applicability:

Availability of and location of source material: For this method to proceed, a plentiful source of dolomite rock is required. These rocks are very common in nature and are often closely associated with many of the sedimentary basins which historically have provided much of the world's coal which in turn has led to the establishment of numerous fossil fuel power stations.

Demand needs: Although the raw materials for this process are readily available in nature, the scale of the required operation, particularly with regard to the amount of NaCl necessary for the process, puts into question the capability of this process to meet the demand of a single 500 MW power plant.

Capacity of technology: With doubt cast as to the ability of this process to satisfy the needs of a single power plant, it is unlikely that this technology can be expanded to fulfil a more global need for sequestration.

Verdict:

Although the basic chemistry and thermodynamics of the process are proven, the volumes of solution, magnitude and cost of the plant to deal with them, and the potential environmental impact of oceanic discharge, render this method unfavourable.

5.3 Process Summaries

Various methods have been put forward for the mineral sequestration of CO_2 utilising a number of differing start products and reaction mechanisms.

In Method 1, the silicate is dissolved in acid to produce $Mg(OH)_2$ which is subsequently carbonated. The products from this reaction are benign, with SiO_2 and $MgCO_3$ produced as solids, the former most likely as a hydrated slurry. These products may be stored in abandoned mines, quarries, or tailings dams. The hydrochloric acid will be recycled in this process, so although a considerable amount will be required there will be negligible environmental impact from this component. The acid is the only additional input to the process.

It has been demonstrated that this route to $MgCO_3$ by the dry carbonation of $Mg(OH)_2$ will be successful in sequestering CO_2 and can potentially be scaled to sequester all the CO_2 from a power plant. This method has been termed the "baseline" process (Wendt 1998(b)) for the carbonation of Mg silicates.

The baseline process as described by Wendt (1998(b)) is:

Dissolution: $Mg_3Si_2O_5(OH)_4 + 6HCl \rightarrow_{aq} 3MgCl_2 + 2SiO_2 + 5H_2O$
Water Recovery I: $MgCl_2.6H_2O + heat \rightarrow MgCl_2.4H_2O + 2H_2O\uparrow$
Water Recovery II: $MgCl_2.4H_2O + heat \rightarrow MgCl_2.2H_2O + 2H_2O\uparrow$
Water Recovery III: $MgCl_2.2H_2O + heat \rightarrow MgCl_2.H_2O + H_2O\uparrow$
Acid Recovery: $MgCl_2.H_2O + heat \rightarrow Mg(OH)Cl + HCl\uparrow$
Hydroxide Formation: $2Mg(OH)Cl \rightarrow_{aq} Mg(OH)_2\downarrow + MgCl_2$
Carbonation: $Mg(OH)_2 + CO_2 \rightarrow_{aq} MgCO_3\downarrow + H_2O$

The only disadvantage of this process is that in order to make $Mg(OH)_2$ from the silicate via the chloride with recycling of the HCl, considerable evaporation of water is required which will be an energy cost to the system. It is also the case that there may not be full conversion to the carbonate because a crust of carbonate will form around the hydroxide particles. This can be improved by using appropriately fine grained $Mg(OH)_2$ which will be obtained by precipitation and there are indications (Lackner *et. al.* 1998) that around 80% conversion can be achieved.

As an alternative way to produce the initial $Mg(OH)_2$, one could start with a concentrated Mg chloride brine (Method 2) and derive the hydroxide from this, liberating a large quantity of HCl. This is the approach envisaged by Dunsmore (1992). In some locations, where there is a shortage of pure Mg silicate rocks, it may actually be preferable to start from such a brine, although the environmental implications of generating and storing vast amounts of acid are daunting. The final carbonation process would be unchanged.

Recently Wendt *et al* (1998) have investigated the possibility of whether their baseline process can be modified to produce alternative routes in which the number of steps required and the overall energy need is reduced. While there exist sufficient data on the baseline process to enable an approximate evaluation of the process from mining the silicate rock to disposing of the solid SiO_2 and $MgCO_3$ products, the viability of the alternative modified processes requires investigation, in particular with regard to kinetic factors. Although the thermodynamics of the various processes can be calculated reasonably easily, the authors who have carried out these initial calculations (Wendt 1998(b)) are fully aware that unfavourable reaction kinetics may render these processes unviable.

The two alternative methods that have been put forward are:

- Dissolution of the silicate rock (e.g. serpentine $Mg_3Si_2O_5(OH)_4$) in a melt of hydrated $MgCl_2$ (Method 3a). It appears that partial dehydration of the hydrated silicate will be required before this dissolution will take place, and
- Direct carbonation of the Mg in the melt to produce $MgCO_3$ (Method 3b). In principle this would be ideal, but would certainly require an elevated pressure of approximately 20 bar of CO_2. Increased pressures up to 100 bar could be utilised, but would reflect in the cost and complexity of the plant.

The problem with the processes which avoid formation of $Mg(OH)_2$ prior to carbonation is that one is essentially using the equilibrium:

$$M^{2+}_{(aq)} + \mathrm{CO}_{2\,(g)} + \mathrm{H_2O}_{(l)} \xrightarrow{\text{eqm}} M\mathrm{CO}_{3(s)} + 2\mathrm{H}^{+}_{(aq)}$$

This equilibrium is very far in favour of the reactants except when the pressure of CO_2 is very large.

Furthermore, the problem of the unknown reaction kinetics means that although the process can be costed at a given set of kinetics, in reality, the reactions may be too slow to be of commercial interest. This effectively means that we can only really consider Method 1 for a full financial appraisal (Section 7).

Experimental investigations of these promising alternative routes should be carried out in order for these to be costed and their feasibility assessed.

Two other methods have also been considered as possible routes for mineral carbonate sequestration.

Method 4 considers the possible use of the reaction between $Ca(OH)_2$ in solution with CO_2 to produce $CaCO_3$. This method has intrinsic drawbacks in that the solubility of $Ca(OH)_2$ is very low and thus large quantities of solution need to be pumped round the plant. Furthermore, the concentration of Ca in silicate rocks is considerably lower than for Mg (thus requiring more feedstock for an equivalent sequestration capability), and the technology for the extraction of Ca from silicate rocks seems to be more poorly documented.

Similarly, Method 5 is based around the Weldon process which utilises a mixture of powdered dolomite with seawater into which CO_2 is introduced under pressure for the production of sodium bicarbonate. This method, although looking attractive thermodynamically and kinetically, has the intrinsic drawback that the process starts with a carbonate as the feed and thus the process is in effect “double accounting” for the CO_2. This factor alone in combination with the huge volumes of solution required, magnitude and cost of the plant to deal with them, and the potential environmental impact of oceanic discharge, render this method unfavourable.

5.4 Conclusions

The above analysis indicates that in order to actually describe a process for storing CO_2 as either Mg or Ca carbonates, and to determine with a reasonable degree of accuracy the cost in terms of cash spent versus proportion of CO_2 sequestered, we must consider processes about which there exist some experimental data.

Unfortunately this rules out some of the most recently suggested methods which are currently at the stage of having been subjected to a thermodynamic analysis. The viability of these processes will no doubt be the subject of future experimental investigations. Indeed the nature or chemistry requires that this be the case as it is very difficult to predict reaction kinetics without some experimental observations.

Consequently, it is only Method 1 that can realistically be evaluated to any degree of certainty, although even this process has several unknowns in terms of form of some of the bi-products, exact temperatures and pressures of reactions, and consistancy of feedstock. The starting material for the hydroxide could be magnesium-rich silicates which are dissolved in HCl to produce $MgCl_2$ in solution which can be converted to the hydroxide with recycling of the HCl in a process described by Lackner and co-workers.

The products of the process are benign solids which will be produced as fine powders ($MgCO_3$) or as a hydrated slurry (SiO_2). These may practically be stored together. It is possible that the $MgCO_3$ may be of some use, although it may not be produced in a particularly pure form on such a large scale. The choice of pure source rocks will minimise the other impurity products (most notably iron) which will appear within the waste stream of the process. The impurities may depend on the geological location.

Finally, previous results indicate that while the overall conversion of silicates to carbonates is exothermic, the actual process will probably require a net heat input, which may represent a significant proportion of the CO_2 actually sequestered. In an effort to counter this, it is also worth considering Method 3b which offers the opportunity of direct carbonation. If kinetically viable, this method should greatly improve the economics of the sequestration process.

6.0 ENVIRONMENTAL AND SOCIAL CONSIDERATIONS

6.1 Introduction

The ability to sequester significant masses of CO_2 in the form of stable mineral compounds with minimal toxicity is extremely attractive as a means of reducing potential increases in the atmospheric concentration of CO_2 and, by direct inference, a reduction in the threat of global warming through the greenhouse effect.

However, of the six methods considered here, all but one require the mining and processing of substantial masses of either magnesium or calcium based rocks. One process requires the pumping of magnesium brines from depth in evaporitic basins. All the methods require significant chemical processing works and secure and safe disposal sites for the solid and/or aqueous final products.

Given the *raison d'etre* of the idea of CO_2 sequestration, it is important that any proposed solutions should not, of themselves, cause major environmental difficulties.

All the processes are considered on the basis of plants capable of sequestering 3Mt CO_2 per year and as such will constitute sizeable operations with significant potential for environmental impacts.

6.2 Regulatory Background

There is growing world-wide awareness of the potential environmental and social consequences attendant upon large scale and/or hazardous development projects. Increasing numbers of countries are adopting legal guidelines whereby projects falling within certain categories of operations, or by virtue of their extent or location, are automatically the subject of some form of environmental investigation.

As an example, within the European Union, as a result of Directive 85/337/EEC as amended by Council Directive 97/11/EC, member states are obliged to conduct an Environmental Impact Assessment (EIA) for those projects defined in Annex 1 of the directive. Annex 2 of the Directive lists types of project for which member states should decide on a national basis whether EIA is required.

Similarly, in countries where a federal system of law applies, such as the USA, environmentally sensitive developments are subject to a raft of Federal (i.e., national) and State (i.e., regional) law. These may be supported by best practice guidelines published by national, regional or other planning bodies. The Australian Federal Environmental Department's Environmental Protection Agency publishes a series of guides which form their "Best Practice Environmental Management in Mining Program".

Where no formal legalised screening parameters are applicable, the United Nations Environment Programme (UNEP) provides a series of checklists enabling identification of those projects which it advises receive detailed investigation in the form of environmental assessment.

In the context of CO_2 sequestration by methods described in this report, the following areas of development should be the subject of screening to determine whether or not formal assessment of their potential environmental impacts would be necessary:

- Quarrying and source materials operations;
- Processing plant installations, and
- Waste/final product disposal.

Major factors to be considered in deciding the need for EIA for quarrying, industrial development and associated linear developments are presented in Tables 6.1 to 6.3.

Many of the environmental concerns regarding linear developments are site specific while others present generic impacts of comparable intensity. Thus, the size of the CO_2 pipeline, for example, would be constant, but its impact on, say, animal migration patterns would be site specific. However, such developments are not considered further in this report.

Table 6.1: Factors In The Screening For EIA Of Quarrying, Mining And On-Site Minerals Processing Projects

	Will the project?
Sources of Impacts	Require the conversion of significant areas of land for surface excavations, mineral processing or waste disposal (e.g. >20 ha)?
	Require significant accommodation or service amenities to support the workforce?
	Require significant volumes of local raw materials, water or energy (significance dependent on availability, conflict with other users, sensitivity of operation etc)?
	Result in significant quantities of construction or mining wastes, or eroded material?
Receptors of Impacts	Undertake excavation, mineral processing, waste disposal or construction of transport infrastructure in areas that support conservation-worthy ecosystems, flora or fauna or areas of historical or cultural importance.
	Require the resettlement or compensation of local people.
	Undertake surface or underground mining in areas prone to high flood recurrence.
Environmental Impacts	Present a pollution risk to the workforce, human settlements, terrestrial or aquatic conservation-worthy ecosystems, flora or fauna or commercial species due to: discharge mining waste water; excessive noise or vibration; deposit and subsequent leaching of contaminated spoil; emission of polluting gases and particulates from processing; accidents from the use or transport of hazardous materials?
	Induce secondary development, agricultural settlements, mineral prospecting, entrepreneurial services for the workforce etc?
Mitigation Measures	Require significant levels of management and training to establish or sustain the project.
	Be likely to require mitigation measures that may result in the project being financially or socially unacceptable.

After: Checklist for Mining and On-site Mineral Processing Projects, UNEP 1997.

Table 6.2: Factors In Screening For EIA Of Industrial Development Projects.

	Will the project:
Sources of Impacts	Require the acquisition or conversion of significant areas of land for industrial production, storage or waste disposal?
	Require significant accommodation or service amenities to support the workforce during construction/operations?
	Require significant volumes of local raw materials, water or energy?
	Result in significant quantities of eroded material, solid or liquid industrial wastes or emissions?
Receptors of impacts	Locate industrial plants, waste treatment facilities, disposal sites or transport infrastructure in areas that support conservation-worthy ecosystems, flora or fauna or areas of historical or cultural importance.
	Require the resettlement or compensation of local people.
Environmental Impacts	Present a significant pollution risk to humans, conservation-worthy ecosystems or species, or commercially significant fish stocks due to: discharge of contaminated industrial effluent; discharge of cooling waters; deposit and leaching of contaminated solid industrial wastes; emission of polluting gasses and particulates; accidents from the use or transport of hazardous wastes?
Mitigation Measures	Require significant levels of management and training to establish or sustain the project.
	Be likely to require mitigation measures that may result in the project being financially or socially unacceptable.

After: Checklist for Industry Projects, UNEP 1997.

Table 6.3: Factors In The Screening For EIA Of Linear Developments.

	Will the project?
Sources of Impacts	Require large volumes of construction materials to be taken from local sources (e.g. gravel, rock, water etc)?
	Result in significant quantities of waste or eroded material?
	Require significant levels of accommodation or service amenities to support the workforce during construction?
Receptors of Impacts	Be routed such that population resettlement or compensation is required?
	Be routed through areas that support conservation-worthy ecosystems, flora or fauna or sites of historical or cultural importance?
	Be routed across major drainage channels or surface water-bodies.?
Environmental Impacts	During construction lead to reductions in the quality of potable water supplies or cause harm to fish and benthic communities, due to the siltation of water bodies?
	Present a danger to local populations due to a significant scale of traffic?
	Create barriers to the movement of conservation-worthy wildlife or livestock?
	Lead to a significant increase in congestion and related smog or noise?
	Present a pollution risk to potable water supplies, or to surface water bodies that support conservation-worthy or commercially significant fish, due to accidents during the transport of hazardous materials?
	Lead to unplanned settlement or access to conservation-worthy ecosystems or natural resources (e.g. agricultural land, timber, minerals, squatter settlements etc)?
Mitigation Measures	Be likely to require mitigation measures that result in the project being financially or socially unacceptable?

After: Checklist for Transport Projects, UNEP 1997.

6.3 Environmental Impacts

It is a given fact that all mechanised quarrying or mining operations and most large scale industrial chemical processing will generate significant environmental impacts. These industries involve a range of operations which, if not suitably managed, may be considered potentially harmful.

With regard to quarrying these include:

- Exploration: drilling, test pits, human impacts;
- Waste/overburden stripping and soil storage;
- Blasting and crushing;
- Transport: traffic and access roads;
- Processing;
- Disposal of end product;
- Back-filling and land raising;
- Off-site disposal: dumping/landfill, off-site landraising, and
- Site restoration and future use.

Operations of concern with regard to the chemical processing development include:

- Exploration, site investigations and earthworks;
- Construction: size, scale, location, visual impact;
- Dust, noise, vibration, CO_2 leaks;
- Chemical use: transport, storage, handling, waste disposal;
- Product handling and disposal, and
- Access road construction, fuel/power supply.

The environmental impacts typically associated with the operation of surface rock mining/quarrying and major industry may be divided into three categories: human concerns regarding the site, human concerns regarding the environment and other environmental effects:

Human concerns regarding the site include workforce facilities which cover food/water supplies, recreation, transport, waste disposal, and workforce training, cultural changes, changed local work pattern, imported work force, cultural sites and archaeology, rights of way, access, and uncontrolled development.

Human concerns regarding the environment include visual impact, loss of lands, end-use, restoration, water courses and wells, noise, vibration, dust, emissions, and disease.

Other environmental effects of quarrying include habitat loss, faunal and floral population changes, hydrology/hydrogeology changes, water quality deterioration including measurement of BOD, COD, suspended solids etc, river flow changes, soil erosion, dusts, recreational disturbance/loss, and access roads, which includes linear development.

Many of these impacts, their existence, significance and mitigation, would be largely site specific. However, it is possible to differentiate between the processes under consideration by virtue of the nature and extent of impacts relating directly to the material sourcing, processing and disposal of a particular process.

6.4 Social Impacts

6.4.1 The Issues

The new industrial activity associated with CO_2 sequestration, quarrying and process activities has the potential for significant social impact. The type, extent and degree of benefits or negative effects will vary with the siting, scale of works, local perception of the proposals and management competency (Wathern, 1988).

Social impacts include changes that affect individuals and groups and the interactions between them. In basic terms they are alterations in the way people live, work, play, relate to each other and organise to meet their needs as well as changes in the values, beliefs and norms that characterise their "group" and guide their individual and collective actions (UNEP 1997).

For the purposes of this study, the presumption is the capacity and capability of the quarry/sequestration plant to process 3 Mt CO_2 per year which equates to a feedstock supply of some 7-9 Mt, which in turn is comparable to the production from a medium-sized modern mining operation.

From such an operation, social impacts can be divided into five main types:

- Economic and fiscal impacts, which include changes in individual, group or government financial standings;
- Health impacts, which include alterations in population health status resulting from biophysical or other changes in the environment;
- Demographic effects such as changes in population numbers and characteristics;
- Cultural resource impacts, which include changes in historical and cultural artefacts and environmental features with religious or ritual significance, and
- Socio-cultural impacts, covering changes in social structures, organisations, relationships and value systems.

The type and extent of cultural resource, socio-cultural and demographic impacts is widely variable. However, a major cause of these effects is economic and fiscal changes. Economic impacts are those effecting per capita income, changes in employment and levels of business activity. Fiscal impacts are the changes in the costs and revenues of the various government or group sectors, typically the result of increases in population placing demands on health, road, sewage, education service provision etc.

Factors affecting economic impacts include the duration of construction and operational periods, workforce requirements for each phase of construction/operation, earnings, skill requirements and its local availability, raw material and other input purchases, capital investment, and local economy characteristics.

Factors affecting fiscal impacts include workforce requirements and the size of investment, the capacity of local infrastructure and service delivery, national or other tax or revenue raising processes, and potential demographic changes resulting from the project.

Benefits from new industrial activity can be assessed on the basis of local value and national/international significance. Quarrying may result in increased local employment and produce material of national importance. Alternatively the development of works in an inappropriate area may blight existing industry/agriculture and place unwarranted pressures on social and physical infrastructures.

The self-evident fact that minerals must be quarried where they occur, the presumption of the CO_2 sequestration plant being in close conjunction with the quarry and the desirability of reasonable proximity to the CO_2 source (a fossil-fuel power-station) will lead to a preliminary site selection. However, a considerable number of social factors will weigh in the assessment of specific site suitability.

While the global view of the need for reducing CO_2 levels will lend support to the general principle of CO_2 sequestration in mineral form, it is clear that considerable forethought will be required for the siting and servicing of processing facilities and quarries if projects are not to be perceived as causing more harm than good. A key factor will be the input from local people and organisations along with their appreciation of the long term benefits of the projects.

It is likely much of the power requirement for the 21st century will be derived from fossil fuels. Much of the increased power generation will be in third world countries attempting to reach first world standards. The developed countries are also expected to increase their energy consumption. Therefore if CO_2 sequestration is to make a significant impact on atmospheric CO_2 levels on a country-by-country responsibility basis, then many sequestration plants will be required, world-wide.

As an example of a potential site for mineral carbonate sequestration, certain areas of the Eastern USA appear ideal, having:

- the desired rock types in abundance;
- local coal-fired power stations;
- coal resources;
- a local history of mining, quarrying and heavy industry;
- higher than average unemployment rates;
- a good skills base;
- existing infrastructure, and
- intellectual appreciation of the benefits of CO_2 sequestration.

Many other locations around the world can be compared on a similar basis.

6.4.2 Cost/Benefit

It is impossible to give a general cost benefit analysis for a quarrying/sequestration complex, too many factors being site specific. What may be perceived as a benefit at one site may be considered an unacceptable cost at another. However, possible costs/benefits include:

Benefits:
- Employment;
- Secondary employment;
- New infrastructure – road, rail, electricity supply;
- Education and welfare gains;
- Medical services, and
- Access to previously inaccessible habitation sites.

Costs:
- Land lost to agriculture;
- Cultural site loss;
- Noise, dust, vibration, air pollution;
- Cultural identity loss through immigrant mixing;
- Enforced re-settlement and/or compensation;
- Soil and water contamination;
- Ground and surface water flow pattern changes;
- Soil erosion, and
- Utilisation of scarce local resources.

No attempt has been made to weigh the cost/benefits of changes to non-human environmental factors. Environmental impacts of mineral-based sequestration projects are considered elsewhere in this report. Attempts to place financial values upon environmental components and factors produce results which are extremely site specific.

6.4.3 Employment

Large scale mining and industrial processing tends to generate employment both through direct work within the incoming industry and secondary employment with businesses servicing the prime industries. The apparent employment benefits to local economies of large scale heavy industry often do not materialise, particularly when such industry is foreign to the local or regional economy. Many of the processes are automated or highly skilled and technicians are likely to be imported. Training of local labour forces may take considerable time, and such workers may be lost to other locally important industry.

Primary industry requires the services of secondary industry for many of the products it uses and services to the industry and staff. However, unless there is an existing service capacity with the appropriate history of involvement in projects of this nature, then the benefits of secondary employment are unlikely to accrue to the quarrying/sequestration site.

Mining, quarrying and heavy industry has historically been seen as the driving force for the growth of employment via supplier and associated industry. Multipliers for the additional jobs generated over and above those of the workforce directly associated with the prime industry have been given at between 1.3 and 5. This figure varies depending on the specific type of industry, its scale, degree of automation and complexity. Development of a CO_2 sequestration facility can be expected to produce some local benefit through pipeline, road, services and building construction and ongoing supply of consumable materials. However, with the exception of the latter item, this will be short-term employment rather than throughout the life-time of the project.

Widespread adoption of this technology may need increased production of mining/quarrying plant and industrial/chemical processing equipment. The benefits of this demand are more likely to be seen in the expansion of current manufacturing facilities than the establishment of new factories of benefit to the quarrying areas.

In conclusion, significant social impacts may be anticipated from the introduction of mineral CO_2 sequestration. Whether these are perceived as beneficial will depend upon site selection, public and government perception, process management and appropriate mitigation measures.

6.5 Process Issues

This section outlines the nature of potential environmental impacts for each process method. Where two methods depend on, for example, similar types and quantities of feedstock material, then the environmental significance is described at some length for the first process but not repeated for the other.

6.5.1 Method 1

Land take/use: The quarry will be moderately large. On the assumption that 3t of rock is required for the sequestration of 1 t CO_2 then the quarrying requirement over 25 years for the sequestration of 3Mt per year will be 225 Mt serpentinite/peridotite. Taking an average specific gravity of 2.9 then this equates to a volume of 77.6 Mm^3, equivalent to 1000 x 1000 x 77.6m. A total quarry footprint of approximately 2 km^2 would allow for quarry face sloping, haul roads, crushing plant, other plant depots etc.

The processing plant can be anticipated to require several hectares for direct and ancillary development associated with the CO_2 sequestration plant. However this land take is included within the 2 km^2 noted above.

The volume required for tailings/waste disposal will be dependant on the form of the materials, their density, and capacity for gravity dewatering and compaction. We can expect some 3t of final products per tonne of CO_2 sequestered. This will comprise approximately 1.9 t $MgCO_3$, 0.9 t of SiO_2, , various iron and other metal oxides and a small mass of lost process water. These figures assume the silica can be removed in a concentrated form from the process stream. Inefficiencies in the silica concentration, resulting in excessive water loss, will increase the volume of waste for disposal. The $MgCO_3$ will be in the form of a dry powder and the silica as a sludge of varying water content, depending of the separation techniques used. The combined waste material is anticipated to have a specific gravity of <2. Therefore, we have some 9Mt of product per year with a minimum volume of some 4.5 Mm^3. Over 25 years this equates to 112.5 Mm^3, a volume some 50% greater than that of the original quarry or equivalent to 1000 x 1000 x 112.5 m.

The disposal and deposition of the waste products poses significant problems. The immediate presumption is to utilise the quarry providing the source rock as the main disposal site. However, there are considerable practical problems related to waste disposal within a site of active workings. These are concerned with the physical stability of the waste, the sterilisation of resources and impingement on the efficient working of the quarry.

In this process, the waste will be a combination of dry powder $MgCO_3$ and a silica sludge of varying water content. Combination of the two would lead to a thickened sludge for disposal. Containment of this waste would require the construction of boundary bunds. It is probable that at least 20% of the quarry extraction, ie 5 years production, working to full projected depth, would be required before any material could be deposited within the quarry. This figure is considered the minimum which would permit adequate void space generation yet allow for infilling with minimum sterilisation of resources and within practical cost and safety limits.

However, there will be a minimum 50% volume excess of materials for disposal above that provided by the finished quarry void. This would require a tailings dam/waste lagoon of volume 1000 x 1000 x 35 m. The provision and filling of such an area would permit the excavation of a potentially sufficient volume of the quarry to make the commencement of backfilling a practical possibility after some 10 years of quarry life. This assumes that no gravity dewatering of the waste product is required before disposal.

At the close of the 25 year project life the site would comprise a tailings dam and a quarry filled with material of very fine particle size. The rate of dewatering, compaction and cementation of the waste materials is currently unknown. Strategies and costs for remediation of the sites would largely depend upon these factors. Therefore experimental work to determine the physical characteristics of the waste is required before a reasoned estimate of site stability, potential future uses and remediation costs can be attempted.

Other potential strategies for waste disposal include the creation of one large tailings dam/lagoon of approximately 2000 x 2000 x 30 metres to receive all the waste products, or the creation of a number of small quarries, effectively encircling the process plant and a small storage lagoon. Here wastes produced during the working of the first quarry would be stored until the completion of this quarry, when working on the second quarry would permit the first to be used for waste storage. This option avoids the difficulties associated with waste disposal within an active quarry but would entail a larger land take and still ultimately require above ground storage of the 50% excess waste material.

Hydrology/hydrogeology: Mine and quarry development is likely to have significant impact upon the surface water (hydrology) and groundwater (hydrogeology) regimes in both the immediate and wider area of the project (CIRIA, 1996).

An extensive, deep quarry is likely to intersect the water-table and therefore risk potential flooding, disruption of normal groundwater flow, and possible contamination of groundwater. Similarly, quarrying activities and the removal of topsoil and overburden may alter the rainfall run-off pattern which may also lead to quarry flooding, increased soil erosion, the diversion, creation or overloading of surface water drainage systems, and reduction in overall water quality. Overall, the degree of impact will vary depending upon the site of the project, but could be potentially severe.

Water movement within serpentinite/peridotite is largely due to fractures rather than intrinsic permeability and therefore these rocks are not considered significant aquifers compared with many sandstones and limestones of high porosity and hydraulic conductivity. However, they may support local well and borehole water supplies. The generation of kilometre scale quarries may be expected to reduce local groundwater supplies through dewatering effects.

Some water will be required for dust suppression purposes and may also be suitable, after treatment, as process water. However, where excess water enters the quarry its disposal requires care. Normal practice is to pump quarry floor water to surface holding tanks to allow for sedimentation/settlement of suspended materials and treatment of any contaminants such as diesel fuel etc. In the case of a serpentinite quarry, much of the finer solids will be siliceous material. Silica is essentially biologically inert, but can cause significant physical damage through non-chemical effects. These include direct abrasion to living organisms, e.g. damage to fish gills, settlement on substrates impacting upon benthic habitats, reduced light penetration of waters and settlement on plants leading to reduced photosynthesis, and impacts on surface water users, people, livestock etc.

When treated, this water may be of sufficient quality and quantity to be of use to the neighbouring population or may then be discharged to surface waters. The chemical parameters of the discharge waters should be as close to those of the receiving water as is practical. Discharges would preferably take place at times of high natural water flows to reduce the proportional impact of the discharge upon the natural flow and chemical/biological regime.

The final waste product of the sequestering process will be a thickened sludge of silica, $MgCO_3$ and iron and other metal oxides. At least a third of the total produced during the life of the project will require disposal in a tailings dam/lagoon with the remainder being equivalent to the quarry void. Due to the fine grain size, this material will dewater only very slowly. Seepage from tailings into groundwater is a major issue with many disposal operations and the nature of the seepage water will require definition. It is generally necessary to complete studies of geochemical and hydrogeological regimes prior to selecting sites and designing the storage facility to enable prediction and minimisation of impacts.

Seepage, inadequate control of excess precipitation and pipeline ruptures offer routes for pollution of surface waters. The nature of the waste fluids and the receiving waters should be determined to permit a management plan for the appropriate treatment of tailings related waters.

Visual impact: The visual impact of quarrying can be largely mitigated by modern design and working methods such that it can be minimal other than within the immediate area of the site. The extensive and widespread nature of appropriate rock deposits should ensure that sites of minimal intrinsic visual sensitivity can be utilised. The capacity for landscaping completed quarries is largely dependant upon the nature of the fill material. In the long term, the fill can be expected to stabilise through dewatering, compaction and cementation effects. However, the timescale required for these processes may preclude immediate postclosure restoration to an earlier landscape form.

The CO_2 sequestration plant will be an extensive development, requiring process of approximately 1000 t of rock material per hour and fluid flows of more than 2000 m^3 over the same period. Typical strategies to minimise the visual intrusion generated by such plants include utilisation of landscape features such as hills, valleys, etc, to shield the plant from critical viewpoints, the creation of bunds or barrier structures or the planting of quick maturing trees and shrubs, and utilisation of appropriately coloured paints and the avoidance of metallic finishes.

Tailings dams are preferably built in valleys, downstream of the quarry/process plant to avoid or minimise pumping and dam construction costs. Here, the scale of the dam will depend on the overall disposal route selected. Nonetheless, all tailings dams are more or less visually intrusive by virtue of their extent, constant angle sides, flatness and, often, the colour of the waste material. Choice of site for the dam will depend largely on the local terrain, hydrology, seismicity, the pattern of urban development and human settlement and the availability of construction materials.

The SiO_2 and the $MgCO_3$ for disposal are both white, although the large volume of iron and other metal oxides for co-disposal will combine to produce a brownish sludge of comparatively low visual impact.

Similar constraints on the restoration of the tailings dam apply as for the quarry.

Noise, vibration and blasting: The main sources of noise and related impacts are associated with the rock quarrying, transport and comminution of the rock material to a size suitable as feedstock for the process plant. The majority of nations involved in large scale mineral workings include provision within their permitting conditions for the minimisation and control of such impacts. Where no such controls exist, then any future projects should be based upon the best practice of countries where such conditions do apply. The scale of operation anticipated for this method does not pose significant problem.

Dusts: All quarrying tends to produce dusts to some degree. However, as these are generally larger than 10 micron they are not considered "respirable" and are usually considered more as a nuisance than a direct health hazard. Such dusts can be minimised by appropriate working practises such as water spraying of haul roads and stockpiles.

Of more concern are the dusts which may be associated with the end products of the sequestration process. These are primarily $MgCO_3$ and SiO_2. Chemically, these products can be considered as largely inert, although their fine-grained nature does create intrinsic handling and disposal difficulties. The $MgCO_3$ will be produced as a fine, <10 micron, dry powder, whilst the SiO_2 is expected to be present as a hydrate with the consistency of thick mud, but again comprising significantly small particles.

The $MgCO_3$ in powder form will be difficult to handle and emplace for disposal. Airborne dusts will be easily generated from such material and would constitute "respirable dusts", i.e., <10 microns. Such dusts are able to penetrate deep into the lungs and cause respiration problems.

Surface evaporation effects would produce silica and $MgCO_3$ dusts on the surface of placed deposits. Again, both would constitute "respirable dusts" and cause lung irritation but, in addition, fine silica can cause the respiratory disease "silicosis". Fine windblown dusts can be a direct nuisance to humans and animals and actively harmful to plants and agriculture. Settlement on leaves may reduce transpiration and reduce photosynthesis through the shading effect.

Deposits of these fine grained materials will have to be actively managed to reduce the generation of dusts. It may prove necessary to moisten or otherwise bind the powder particles for transport from the sequestration plant to disposal. Similar action will be needed to prevent the escape of surface dusts from waste disposal sites.

CO_2 leakage: Carbon dioxide is heavier than air and an asphyxiant. Escaping CO_2 can settle into pools when air movement and mixing is slow. These pools can present a serious threat of asphyxiation to both man and animals. However, appropriate design and regulatory control of the construction and operation of the CO_2 pipeline and the processing plant should prevent any undue risk.

Disposal method and final soil stability: The solid $MgCO_3$ and silica will require disposal in an extensive tailings dam with ongoing management to prevent the formation and dispersal of windblown dusts. The final stability of the site will depend upon the form of the material, its compressibility, cementation characteristics and water content. Experimentation will be required to determine these factors and their effects.

6.5.2 Method 2

Land take/use: This method depends upon the utilisation of $MgCl_2$ rich brines as the initial source material for $Mg(OH)_2$ rather than upon a silicate rock. Therefore, there is no land loss through quarrying. However, sufficient pumping stations will need to be constructed to consistently supply the process plant with some 2000 t per hour of saturated $MgCl_2$ solution. The number of pumps will depend on the availability and concentration of the $MgCl_2$ brine, with pipelines being constructed to link them to the process plant.

For the process plant, infrastructure needs and the scale of the process indicate a likely land take of comparable but somewhat larger scale than that required for Method 1 discussed earlier.

This method of CO_2 sequestration poses a number of significant and unique waste disposal problems. Here the entire solids product must be disposed in a tailings dam/settlement lagoon. Therefore, over the 25 year life of the project, there will be some 5.7 Mt, or approximately 3 Mm^3, of $MgCO_3$ in the form of a very fine dry powder for disposal. This is equivalent to 680 t per hour for the sequestration target of 3 Mt per year of CO_2 and would require the creation of one large tailings dam/lagoon of approximately 2000 x 2000 x 30 metres to receive all the waste products. It may be necessary to add water to the powder to facilitate transport and emplacement within the tailings area and minimise dust production.

Facilities would also be needed for the disposal of excessive volumes of HCl, a major by-product of the sequestration process. For each tonne of CO_2 sequestered, 1.7 t of HCl is produced, equivalent to 5.1 Mt a year for the sequestration target of 3Mt per year or 680 tonnes per hour. The only apparent option for disposal of this material would be re-injection down the brine wells, a comparable technology with that used by the oil and gas production companies to maintain the pressure and thus flow from their hydrocarbon wells. However, the consequences of pumping large volumes of acid into inherently unstable evaporite rocks are unpredictable. Disposal of the HCl by release to surface waters, freshwater or sea, is environmentally unacceptable.

This process also requires the disposal of almost 3 tonnes of water, as steam, for each tonne of carbon dioxide sequestered, or 975 t per hour. Some of the energy involved in steam production may be recaptured as heat and the resulting water should not present significant re-use/disposal problems.

Hydrology/hydrogeology: This process produces a dry $MgCO_3$ powder, vast quantities of hydrochloric acid and steam plus an unknown quantity and type of other products dependent on the composition of the original brine. An appropriate disposal route must be found for the HCl, other than disposal to surface or groundwaters. The addition of substantial amounts (approximately 680 t per hour) of HCl to either sea or surface waters is unacceptable. The effects on the water regime of initial brine extraction (12 Mm^3 per year minimum for 3Mt CO_2) and of pumping the acid back into the $MgCl_2$ reservoirs among reactive evaporite rocks, are beyond the scope of this study, but may be expected to be substantial.

Approximately 1000 m^3 per hour of water may be produced through the condensation of steam from the early stages of the sequestration process. This water may become available for human, agriculture or business use, but is unlikely to pose a serious disposal problem.

The process facility will have a substantial footprint and a precipitation drainage system would need to be provided. Such drainage water may be contaminated by solids, escaped hydrocarbons and other chemicals and so would require treatment before release to surface waters. The process facility should be sited such that it does not directly interfere with surface drainage water patterns. These comments regarding the process plant apply to all the sequestration methods under consideration.

Land stability/subsidence: The $MgCl_2$ brines proposed for use in this method are often derived from evaporitic rock sequences, as well as from suitable aquifer rocks. The evaporites are chemically and physically unstable, exhibiting plastic behaviour under comparatively low pressures. This method requires the extraction of 12 Mm^3 of pure, saturated $MgCl_2$ brine to meet the sequestration target of 3Mt CO_2 per year. It seems improbable that the extraction of this volume of material (300 Mm^3 over 25 years) will not affect surface stability and generate widespread subsidence.

Visual Impact: A sequestration plant based upon $MgCl_2$ brine would have considerable visual impact. Whilst there is no quarry for this process, there would be a large chemical processing plant, an unknown but substantial number of pump stations and a network of pipelines to carry the brine, and possibly hydrochloric acid, to and from the process plant.

The tailings dam/waste repository would be some four times larger than that required for Method 1, whilst the same comments regarding the minimisation of the visual impact of the process plant and the waste site apply as in the case of Method 1.

Noise and vibration: Noise and vibration levels are directly associated with pump size and capacity and can be expected to vary with the depth and capacity of the brine aquifers being worked. Noise levels would be effectively doubled if the option is taken to dispose of the acid generated in the sequestration process by re-injecting it into the aquifer.

Dusts: The end product, $MgCO_3$, will be produced as a very fine powder of less than 10 micron particle size. Whilst the product is considered essentially non-toxic, the particle size is such as to be considered “respirable”, i.e., capable of entering the fine structures of the lungs and causing irritation and reduced respiratory efficiency. To counter this, handling and waste emplacement may require a water addition to the powder to reduce dusts and improve its handling characteristics. The waste deposit sites will need to be managed to prevent both the generation and escape of undue levels of dusts.

CO_2 Leakage: The same comments apply as recorded under Method 1 (above).

Contaminants: Brine composition will vary considerably from site to site, and thus careful monitoring will be required to determine levels of potential contaminant elements which may prove problematic for safe disposal.

Disposal method and final soil stability: The solid $MgCO_3$ will require disposal in an extensive tailings dam with ongoing management to prevent the formation and dispersal of windblown dusts. The final stability of the site will depend upon the form of the material, its compressibility, cementation characteristics and water content. Experimentation will be required to determine these factors and their effects.

The difficulties in finding an acceptable disposal route for the HCl produced by this process appears, at this stage, a fatal flaw.

6.5.3 Method 3a

Land take/use: The quarry requirements will be as for Method 1.

The plant is of comparable complexity to Method 1, although the footprint may be somewhat smaller as there is less requirement for water evaporation.

The end product of the sequestration process is a mixture of $MgCO_3$ and SiO_2 in dry, powder form in similar quantities to those produced in Method 1, thus providing similar environmental problems. However, this method produces excess water for disposal of the order of 15% by weight of the mineral end product which might beneficially be incorporated with the mineral waste to assist in reducing dust generation during transport and emplacement.

Hydrology/hydrogeology: Method 3a is comparable with Method 1 in that quarry development is likely to have significant impact upon the surface water (hydrology) and groundwater (hydrogeology) regimes in both the immediate and wider area of the project.

The final waste product of the sequestering process will be either a powder or a thickened sludge of silica, $MgCO_3$ and iron and other metal oxides. At least a third of the total volume produced during the life of the project will need disposal in a tailings dam/lagoon with the remainder being equivalent to the quarry void. Seepage from tailings and percolation through tailings into groundwater is a major issue with many disposal operations and the nature of any seepage water will require definition.

There will be an excess of water for disposal from the processing plant equivalent to approximately 15% by weight of the CO_2 sequestered, equivalent to 53 t per hour. This may be beneficially used to dampen the $MgCO_3$ and SiO_2 products of sequestration to assist with waste emplacement at the disposal site. However, any accidental releases must be treated to an acceptable level before disposal to surface waters. Similarly, run-off associated with the process plant should receive adequate treatment and monitoring to avoid contamination of surface waters.

Visual impact: The extent of development for this method of sequestration is comparable with that required for Method 1 and as such, similar comments apply.

Noise, vibration and blasting: The extent of development for this method of sequestration is comparable with that required for Method 1 and as such similar comments apply.

Dusts: Dust problems relating to the quarrying, comminution of rock material, transport, and disposal of final products are the same as those for Method 1 and as such similar comments apply.

CO_2 leakage: The same comments apply as to Method 1.

Disposal method and final soil stability: The solid $MgCO_3$ and silica will require disposal in an extensive tailings dam or within the worked-out quarry and a lesser tailings dam with ongoing management to prevent the formation and dispersal of windblown dusts. The final stability of the site will depend upon the form of the material, its compressibility, cementation characteristics and water content.

6.5.4 Method 3b

This variation of Method 3 has been proposed to reduce the evaporation requirements of Method 3a and Methods 1 and 2. The process involves the use of Magnesium silicate rocks which are dissolved in a hydrated $MgCl_2$ melt and directly reacted with CO_2. The end products are of a similar form as in Method 3 with the exception of approximately twice as much excess water i.e., approximately 30% by weight per tonne of CO_2 sequestered. Again, this may be utilised in the handling of the end products.

Land take for the processing plant may be smaller than Methods 1 and 3a due to the avoidance of water evaporation needs and the apparently simpler separation of waste products from recycled materials. However, the overall footprint of the development is unlikely to be significantly smaller than these other methods.

In all other respects the same comments made regarding the environmental impacts of Methods 1 and 3a can be applied to Method 3b.

6.5.5 Method 4

Land take/use: The land take associated with this process is considerably higher than that associated with magnesium silicate or magnesium chloride brine based processes. This method of CO_2 sequestration is based upon a calcium silicate source rock which are considerably more dilute than their magnesium counterparts, requiring in excess of 10 t per tonne CO_2 . This will be reflected in the areal extent of quarry workings which will require over the life of the mine, extraction of approximately 1000 Mt of rock. This equates to a quarry extending over 5 km^2 and 100 m deep which is a substantially larger footprint than that required for magnesium silicate based processes.

In addition, over the 25 year life of the project this process will generate some 1100 Mt of solid waste products for disposal. As with Method 1, it may be possible to utilise the quarry for disposal of some of the material. However, at a presumed specific gravity of <2 there will be a waste materials volume of some 550 Mm^3. This is 50 Mm^3 greater than the volume of the quarry and similar limitations apply to the deposit of waste within the quarry as discussed for Method 1. Alternatively, if all the waste was directed to a tailings dam/lagoon of 25 m depth, then an area of 22 km^2 would be required. This is a significant increase over other rock based methods.

With regard to the process plant, two routes are available for the sequestration of CO_2 after the initial production of $Ca(OH)_2$ from the calcium silicate rock. It may be carbonated dry as with the production of $MgCO_3$, or one could carbonate a saturated solution of $Ca(OH)_2$ (limewater). In the first case, the plant footprint would be comparable with that ascribed to Method 1, whilst the second case generates a very much larger footprint, based upon the use of 500,000 t water per hour of CO_2 sequestration for production of the saturated limewater. This second option would require reliable water sources, very extensive water treatment and reservoir facilities, and appropriate plant to mix the limewater solution, react the CO_2 and then filter the $CaCO_3$ product for disposal.

Hydrology/hydrogeology: The effects of quarrying and waste disposal would be similar to Method 1, although on a larger scale. Also, the greater footprint associated with the wet, limewater, process route would entail more intensive run-off control and management systems. The volumes of fresh process water required for the production of limewater for the wet version of this sequestration process would place major demands on available water resources at most sites. It may be that this demand alone be considered a fatal flaw for the application of this process.

Visual impact: The visual impact of a site operating this process would probably be greater than other methods considered earlier as a result of the increased quarry size and treatment facilities.

Noise, vibration, blasting: The impacts arising from rock production and processing would be similar to those described for Method 1.

Dusts: The carbonation of dry $Ca(OH)_2$ powder produces similar fine dust materials as Method 1, i.e., silica and $CaCO_3$. The calcium carbonate is comparable with $MgCO_3$ produced in Method 1 and again is considered to be essentially non-toxic but a potential irritant. Silica dusts are potentially harmful, posing a risk of the respiratory disease silicosis. The wet, limewater, route to carbonation produces the same amount of silica and in the same form as the dry process but here the $CaCO_3$ product would be in the form of a damp sludge. This would alleviate one source of dust at the processing and waste emplacement stages of the operation. However, as with other methods of sequestration considered, the waste material would need management to prevent the occurrence and distribution of wind blown dusts arising as the waste dries.

CO_2 leakage: All the processes present a similar risk of CO_2 leakage.

6.5.6 Method 5

Land take/use: This process utilises dolomite which is a double carbonate of magnesium and calcium ($CaMg(CO_3)_2$). Dolomite has a theoretical content of 45.7% $MgCO_3$ and approximately 1.9 t is required for each tonne of CO_2 sequestered. Therefore, approximately 4 t of dolomite is required for each tonne of CO_2 sequestered, equating to 33 Mt over the project life. At a specific gravity of approximately 2.8, a quarry void of 107 Mm^3 or 1000 x 1000 x 107 m is produced. This is comparable to that needed for Method 1, and thus similar comments apply. The process also requires a substantial supply of seawater, equivalent to approximately 15,000 t per hour.

The footprint for the processing plant is likely to be substantially greater than those previously discussed, other than the wet, limewater, version of Method 4. The process requires the reaction of some 22,000 t per hour of reactants, nearly an order of magnitude greater than the other methods. The process also requires the evaporation of approximately 12,000 m^3 of water per hour. Equipment necessary for this evaporation can be expected to contribute substantially to the plant land-take. Seawater pumping, filtering and storage facilities will also be required, along with storage facilities to accommodate NaCl for the required additional input into the main reaction chamber.

Working to the annual target of 3Mt CO_2 per year, this process produces hourly approximately 1400 t $NaHCO_3$ and 800 t $CaCO_3$, as solids; 820 t of $MgCl_2$, 756 t of NaCl and 1500 t of water; and 12,300 t of water as an evaporate. The calcium carbonate may be returned as waste to the quarry with the NaHCO3, or, if impractical, to a tailings dam, as discussed under Method 1. The evaporate water may be re-condensed and made available for other, non-process related uses.

Sodium chloride and $MgCl_2$ would be disposed of to the ocean while the $NaHCO_3$ may be stored dry or disposed of at sea. Sodium bicarbonate is very soluble in fresh or rainwater and, in the long term, dry stored material may be expected to return to the sea through dissolution, surface and groundwater transport.

Sea disposal of $CaCO_3$ is unlikely to be chemically sensitive, but the question of potential siltation would need to be addressed. Disposal of NaCl to sea would merely constitute the return of part of the salt removed in the first stage of the process where seawater is used as the supporting medium for the dolomite suspension. The Cl ion contribution from the $MgCl_2$ for disposal was also originally sea-derived but the magnesium ion input would constitute an increase above current naturally occurring levels. Average sea magnesium level increases would be negligible, but could be significant on a local scale, adjacent to the waste input.

The disposal of $NaHCO_3$ to the sea would represent the return of sodium, but an increase in the bicarbonate ion concentration, leading to elevation of the pH level. Marine creatures are varyingly sensitive to changes in pH. There is current concern about the widespread decline of coral-reefs which has been tentatively ascribed to the lowering of seawater pH levels due to acidification through CO_2 absorption. If this is shown to be the case, then anthropogenic elevation of sea pH levels through $NaHCO_3$ addition could prove beneficial. However, problems associated with localised excessive pH rise due to point source injection of the $NaHCO_3$ would need to be addressed. The best option would appear to be injection into fast moving deep water currents, so offering rapid dispersal and mixing, although this would require evaluation as to the environmental effects and efficiency.

Hydrology/hydrogeology: The hydrological effects of quarrying, processing and waste disposal would be similar to Method 1, but care would be needed in selecting an appropriate disposal route for the 12,000 t per hour of water produced through evaporation if this is recondensed.

Visual Impacts: The visual impact of quarrying can be envisaged as being similar to that produced by Method 1, although the nature of the process is such that the site should be adjacent to the coast to permit use of seawater and disposal of wastes back to the ocean. Industrial developments near coasts have particular problems regarding visual intrusion due to the generally open nature of the terrain. This is further exacerbated in comparison with the other processes under discussion by virtue of the scale of the development required for Method 5. The process plant footprint may be expected to be significantly greater than other processes due to the volumes of material to be reacted, the need for saltwater pumping and storage facilities, the need for a NaCl store and substantial water evaporation facilities.

If the “dry” disposal route for $NaHCO_3$ is taken, i.e., disposal to land, then the volume and mass of solid wastes is likely to be approximately 30% greater than that of the excavated dolomite. It may be feasible to utilise the quarry for disposal purposes, but this can be problematic as discussed under Method 1. In any event, it will be necessary to accommodate approximately 75 Mt of $CaCO_3$ and $NaHCO_3$ above the potential quarry capacity, whilst the scale of the tailings dam will depend on the overall disposal route selected.

Noise, vibration and blasting: The main sources of noise and related impacts are associated with the rock quarrying, transport and comminution as described under Method 1. In addition, pumps capable of handling some 15,000 t per hour of seawater would be required.

Dusts: Unlike Methods 1, 3a, 3b and 4 previously discussed, there is no production of silica in this process and dolomite dust is generally considered as non-toxic. Dusts can be minimised by appropriate working practises such as water spraying of haul roads and stockpiles.

CO_2 leakage: All the processes present a similar risk of CO_2 leakage.

Disposal method and final soil stability: If the “dry” disposal route is followed then the solid $CaCO_3$ and $NaHCO_3$ will require disposal in an extensive tailings dam or within the worked-out quarry and a lesser tailings dam with ongoing management to prevent the formation and dispersal of windblown dusts and to restrict the ingress of water. The final stability of the site will depend upon the form of the material, its compressibility, cementation characteristics and water content. However, the high solubility of $NaHCO_3$ is such that it will easily go into solution under the influence of rainwater and other infiltrating water sources. This tendency to dissolution will adversely affect the ground stability and seriously restrict potential after-use of the disposal site.

6.6 Conclusions

The environmental and social implications of large scale open pit mining or extensive pumping and re-injection facilities, in combination with the manufacture and operation of a large chemical plant with associated substantial tailings disposal, are considerable. It follows that all the methods for mineral sequestration of carbon dioxide present significant potential for adverse environmental impacts, which are comparable with the issues faced by similar sized modern quarrying/mining operations.

This study has indicated that in general, the process routes using magnesium silicate as a feedstock offer the least environmental problems, although a number of issues have been highlighted which require comment:

- Many of the environmental and social impacts of a particular process are common, although precise estimation of these parameters will be determined on a site specific basis;
- Suitable sites for development should only be chosen following a full Environmental Impact Assessment based on national law or appropriate United Nations guidelines;
- None of the processes, other than Method 2, require the disposal of unduly hazardous material, although the removal and proper disposal of silica, which is intrinsic to all methods involving the dissolution of silicate rocks, requires careful planning and administration;
- Final disposal methods and sites will vary with the nature and quantity of waste materials. Lack of knowledge regarding the physical form and behaviour of the end products hinders assessment of disposal site restoration and re-use potential;
- The process plant, though sizeable, presents no significant site restoration problems, as inputs and outputs are generally of low toxicity;
- Significant quantities of metal oxides will be produced with the mineral carbonate which may be utilised as a beneficial bi-product, and
- Mitigation measures associated with the mineral extraction industry would be applicable to mineral carbonate sequestration operations.

7.0 FEASIBILITY STUDY FOR THE BASELINE APPROACH

7.1 Introduction

The conclusions from Section 5 clearly demonstrate that without sufficient experimental data, it is not possible to undertake a detailed investigation, particularly with regard to the cost and efficiency of a process. Thus, it has been shown that only Method 1 could be viably taken to feasibility level, as both thermodynamic and kinetic data are available in conjunction with a theoretical understanding of the process.

However, although Method 1 is better understood than the alternatives, it still presents several unknowns including the form of some of the bi-products, exact temperatures and pressures of reactions, and consistency of feedstock.

In contrast, a high degree of certainty can be placed on sourcing the raw materials, mining and early stage processing logistics and costs, and the environmental and social impacts that such an operation would entail. As Methods 1 and 3b differ only in the tonnage required, these issues will be dealt with together in this section. However, the exact configuration of the plant, working parameters, and potential outputs, can only be estimated, based on the best available data.

Therefore, in order to maximise the accuracy and relevance of the study with regard to costs, it is important that the feasibility study is site specific, or at least, region specific.

To this end, a proposed site for the sequestration plant has been chosen in northeast USA, as this region contains a large number of coal-fired power stations and is relatively close to many of the ultramafic rock units present within the Appalachian Mountain chain.

Thus, all cost estimates provided for the process will be US$ based, and the environmental and social impacts will be discussed with regard to US legislation. Clearly, such a feasibility approach would not therefore be automatically applicable to other areas of the world without considerable modification of cost and policy.

7.2 Source of Raw Materials

Northeast USA represents a typical target area for the establishment of a CO_2 sequestration plant as the historically productive coalfields of this region have encouraged the development of numerous coal-fired power plants.

In addition, as previously discussed in Section 2, ultramafic rocks are relatively common along the Appalachian Mountain chain which extends from the Carolinas in southern USA, through the eastern seaboard, to Newfoundland and beyond. Clearly, only a small percentage of this variable suite of rocks is suitable for the requirements of the sequestration process, and therefore for the purposes of this feasibility study, one particular area has been selected for discussion.

The assemblage of mafic and ultramafic rocks known as the Baltimore Complex has been extensively studied by many authors, although a good summary paper has been produced by Morgan (1977). The complex, which straddles Virginia, Maryland and Pennsylvania, is one of the largest associations of such rocks in the Appalachians within the USA.

The geology of the Complex is reasonably well known and has been divided into four principal units:

- Serpentinised peridotite including dunite with podiform chromite and pyroxenite;
- Gabbro, which in some areas also contains serpentinite layers;
- Quartz gabbro and diorite, and
- Volcanic rocks.

The former three units can be considered as part of a large layered cumulate body, although the whole suite of rocks has been recognised as part of an ophiolite complex which extends for approximately 150 km from southern Pennsylvania through to northern Virginia.

In more detail, the serpentinised ultramafic rocks derived from dunite and peridotite form a continuous unit, appropriately termed the State Line area, at the base of a gabbro mass which occurs for about 30 km from the northeast end of the complex, straddling the Pennsylvania – Maryland border (Figure 7.1). Other, smaller units occur sporadically in a southwesterly direction towards the Virginia border.

Figure 7.1 Location of Baltimore Complex in Northeast USA

Although small chromite lenses occur throughout the belt, the State Line area in particular has been the site of considerable chromite extraction, which during the 19th century yielded plentiful supplies of the metal.

Compositionally, dunite is the parent rock for much of the serpentinite belt in the State Line area, as well as in the more isolated ultramafic bodies further to the southwest. Chemical analyses of these rocks reveal a relatively uniform composition and a high degree of serpentinisation. Table 7.1 shows three typical analyses of the major constituent oxides.

Table 7.1: Serpentinised Dunite Analyses (%) From The Baltimore Complex

Sample Number	1	2	3
SiO_2	40.06	40.70	40.00
Al_2O_3	1.37	0.80	1.50
Fe_2O_3	3.02	7.80	4.90
FeO	3.43	1.20	2.50
MgO	**39.02**	**36.40**	**37.60**
CaO	-	0.09	0.31
MnO	0.09	0.08	0.12
Cr_2O_3	0.20	-	-
NiO	0.71	-	-

Note: These samples also carry minor amounts of Na_2O, TiO_2, P_2O_5, and in excess of 12% water of crystallisation.

Data from Table 7.1 indicates that the MgO content of the three samples is relatively similar, varying from approximately 36 – 39%, whereas the largest differences occur within the iron oxide contents, which show a range from 6.45 – 9.00%. In addition, highly variable amounts of chromium and nickel are also present which need to be accounted for within the sequestration process.

As a requirement of a detailed, fully costed study, an “average” feedstock composition must be assumed. Thus, using the data from Table 2.2 which defines the MgO content of a number of serpentinite bodies, analyses of several other serpentinite bodies (Goff *et al*, 1997), and data from Table 7.1, a representitive composition for a serpentinite can be Table 7.2 defines the rock specification that has been used for the process route calculations:

Table 7.2: Serpentinite Specification Used For Feasibility Study

MgO	Fe_2O_3	FeO	MnO	NiO	Cr_2O_3	SiO_2	SG
35%	2.5%	6.5%	0.13%	0.3%	0.4%	41.0%	2.9

As a final note, although no direct tonnages are known for the amount of suitable sequestering material available within the Baltimore Complex, it is believed that this resource is more than sufficient to satisfy the demand from a number of sequestration plants.

7.3 Mining and Primary Processing

For the envisaged development site in northeast USA, an annual open pit serpentinite production of approximately 13 and 8 Mt have been selected to reflect the tonnages required to satisfy the needs of Methods 1 and 3b respectively.

For the purposes of this study, it is assumed that the occurrence of the ultramafic rocks are such that no allowance has to be made for any waste stripping other than minimal surface detritus. In addition, the serpentinite is expected to be relatively massive with respect to the surrounding country rock, so that all rock drilled and blasted is considered to be ore for the sequestration process.

The construction and operation of large scale open pit mining operations and their associated costs are well documented in Western terms (Mining Cost Service, 1998; Pinock, Allen & Holt, 1989; Noakes and Lanz, 1993). Variations will occur according to a number of differing parameters but a generic case is assumed for this study.

7.3.1 Open Pit Mining Parameters

For this example we have assumed costs based on Western equipment and labour and more importantly, Western statutory rules and regulations for the mining operations and environmental controls.

This study provides an indication of the costs associated with an 8 or a 13 Mt per year serpentinite operation, the throughput being dependent on which process method is adopted. The mine will operate for 312 days per year on a two shift basis.

The geotechnical response of serpentinite is often variable, but for the purposes of this study will be classed as a relatively weak rock. Paventi et al (1996) considered the geomechanical characteristics of variably serpentinised peridotites at the underground Birchtree Mine in Canada. They found that the serpentinised peridotites were soft, with generally low to moderate strength, whilst the less altered peridotites were generally competent rocks.

This somewhat arbitrary classification allows an estimate of the pit slope angle to be made and associated bench height for mining purposes which has been estimated at 6.0 m for the smaller pit to 7.0 m for the larger. Both pit designs have a proposed slope angle of 45^0.

Costs have been assumed as being applicable to North America with electricity and fuel costs of 5c per kWh and 20c per litre respectively. Costs vary around the world for these consumables, and thus a conservative approach has been taken for these figures.

A list of the likely parameters is provided in Table 7.3.

Table 7.3: Open Pit Mining Parameters

Parameter	**8.0 Mtpa**	**13.0 Mtpa**
Production, tpd	25,720	41,750
Average Haul Distance, metres	1,000	1,700
Days of operation per year	312	312
Powder factor, kg per tonne	0.25	0.25
Haul road construction, m	2,300	2,546
Bench height, m	6.0	7.0
SG, t per m^3	2.9	2.9
Geomechanical Properties	Weak	Weak
Haul gradient within pit	+10%	+10%
Haul gradient to plant	0%	0%

7.3.2 Mining Costs

The estimate of mining costs includes the following parameters:

- Drilling and blasting of all serpentinite ore and removal of overburden (if present);
- Hauling of the product to the sequestration plant site;
- Construction and installation of all facilities necessary for the operation, maintenance and repair of all equipment;
- Offices and other accommodation as appropriate, and
- All labour, material and equipment operation costs incurred at the mine, including supervision, administration and on-site management.

However, excluded from the estimate are permitting and environmental analysis costs, provision of access roads, powerlines, pipelines or railroads to the mine, taxes (if applicable), and employee townsite construction (it is assumed that accommodation is to be found nearby).

Capital Costs: The capital costs include all the pre-production development and acquisition, installation or construction of all equipment and facilities necessary to operate the mine at the full design capacity (Table 7.4 and 7.5).

The mine is assumed to be in an area of moderate relief with a temperate climate. Haul road widths will range from 12 m to 25 m depending on the size of the haul trucks.

Table 7.4: Major Capital Equipment for Various Mine Models

Capital Item	8.0 Mtpa	13.0 Mtpa
Equipment:		
Hydraulic/cable shovels	1 x 4.5 m^3	1 x 13.8 m^3
Front end loaders	2 x 5.4 m^3	1 x 13.0 m^3
Rear-dump trucks	9 x 52.6 t	8 x 86.2 t
Rotary drills	2 x 17.15 cm	2 x 20.2 cm
Bulldozers	4 x 210 kW	6 x 210 kW
Graders	1 x 150 kW	1 x 150 kW
Service/Tyre Trucks	5 x 11,000 kg gw	5 x 11,000 kg gw
Anfo loaders	1 x 450 kg/min	1 x 450 kg/min
Small trucks	6	9
Buildings:		
Maintenance shop, m^2	900	1150
Offices, m^2	640	870
Warehouses, m^2	425	900
ANFO (explosives) storage, m^3	47	90
Labour changehouses, m^2	350	390

In addition, other smaller capital items such as secondary drills, backhoes, cranes and various other light plant are required.

For the costing process, the models used are normally associated with mine operations over a 10 year life. It is assumed that the average life of a coal fired power station may be 25 years and thus the mine will be costed on the same basis. Accordingly, a capital replacement programme will need to be incorporated into the cost structure.

The replacement allowances for mobile equipment are based on their total operating hours. In good operating conditions the following replacement life can be expected:

Trucks	30,000 hrs
Dozers	20,000 hrs
Drills	80,000 hrs
Excavators	25,000 hrs

The total working hours per annum for each category of equipment will vary according to their role, but can be expected to lie in the range 4,500 - 5,000. The trucks can be expected to require replacement after approximately 6 years whilst the drill will only need replacing after approximately 15 years.

Table 7.5: Capital Cost Per Element

Capital Cost Element (US$M)	8.0 Mtpa	13.0 Mtpa
Equipment	12.9	20
Haul roads/Site Work	1.0	1.32
Pre-production preparation	0.62	0.65
Buildings	2.1	2.9
Electrical System	0.082	0.151
Working Capital	1.6	2.5
Engineer and Management	3.0	4.5
Contingency	2.1	2.3
TOTAL	**23.4**	**34.32**

No allowance has been made for any major infrastructure requirements in providing either power or access to the mine site. It is assumed for this study that water, power and main vehicular access are at or very close to the mine site, and in turn, are not deemed to be the responsibility of the mine owner/operator.

Operating Costs: The mine operating costs will include all labour, material, supply and equipment operating costs incurred at the mine site, including supervision, administration and on-site management (Table 7.6 and 7.7). Labour costs are common to most North American mines.

A number of specific commodity prices have been assumed for the study, namely:

Item	Cost $
Diesel	0.20/l
Electricity	0.05/kWh
ANFO (explosives)	0.44/kg

Table 7.6: Typical Mine Operating Cost Elements

Operating Cost Element	8.0 Mtpa	13.0 Mtpa
Hourly labour	60 persons	100
Salaried Personnel	25 persons	34
Supply Requirements/d:		
Diesel	12,250 litres	14,309
Electricity	1,598 kWh	14,752*
ANFO (explosives)	6,500 kg	10,200

*Note: Figure reflects use of Electric Shovel

Table 7.7: Typical Mine Operating Costs

Operating Cost Element ($ per t)	**8.0 Mtpa**	**13.0 Mtpa**
Supplies and Materials	0.50	0.50
Labour	0.51	0.42
Administration	0.21	0.16
Sundry Items	0.12	0.11
Total Operating Cost	**1.34**	**1.19**

These costs assume run of mine (ROM) material is provided to a crushing plant situated at the plant site.

7.3.3 Primary Processing

The crushing and grinding circuit for the treatment of approximately 1500 tph of ore is expected to be straightforward, following the format as outlined in Section 3.

The energy required for crushing and grinding rocks or minerals to a size suitable for beneficiation or reaction is determined using equations originally developed by Bond (1952).

The basic equation is

$$P = 10Wi \ * (1/\sqrt{P_{80}}) - (1/\sqrt{F_{80}})$$

where P = Power required
Wi = Bond Work Index
P_{80} = 80% passing size of the product
F_{80} = 80% passing size of feed.

The "80% passing size" is the size at which 80% by weight of the sample is finer than.

This equation can be further modified using "Efficiency Factors" which relate to the parameters such as finess of grind, size of mill, number of grinding stages, etc.

The crushing and grinding work indices are obtained from laboratory test data and then inserted in the Bond equation. The power consumed during crushing is generally considerably less than is consumed in grinding.

The power required to grind to a nominal 80% passing 100 μm can be determined using the Bond equation and making the following assumptions:

- The Bond ball mill work Index is 13.0 kWhr per tonne (appropriate for a serpentinite feed);
- The rock enters the comminution circuit at a size of 80% passing 50 cm, and

- The 80% passing size is 75 µm (100% passing 100 µm).

The power requirement is thus calculated as 15.45 kWhr/tonne.

Capital cost estimate: the cost of the stockpile area, crushing and grinding plant for a 1,500 t/h operation is estimated at $62 million, whilst that for the smaller throughput (916 t/h) used in Method 3b is $46 million. These figures are based on the Pinock, Allen & Holt, 1989 cost model, modified by the “six tenths” rule.

The costs assume that the plant operates 350 days per year. The grinding process will be undertaken wet since this is more energy efficient than dry grinding.

Operating cost estimate: Using a power cost of US$0.05 per kWhr and standard process cost models, comminution costs can be calculated (Table 7.8).

Table 7.8: Comminution Costs

Item	**Cost ($/t)**
Electrical energy	0.77
Grinding media	0.60
Labour	0.57
Repair materials and supplies	0.28
Total	**2.22**

7.4 Process Plant

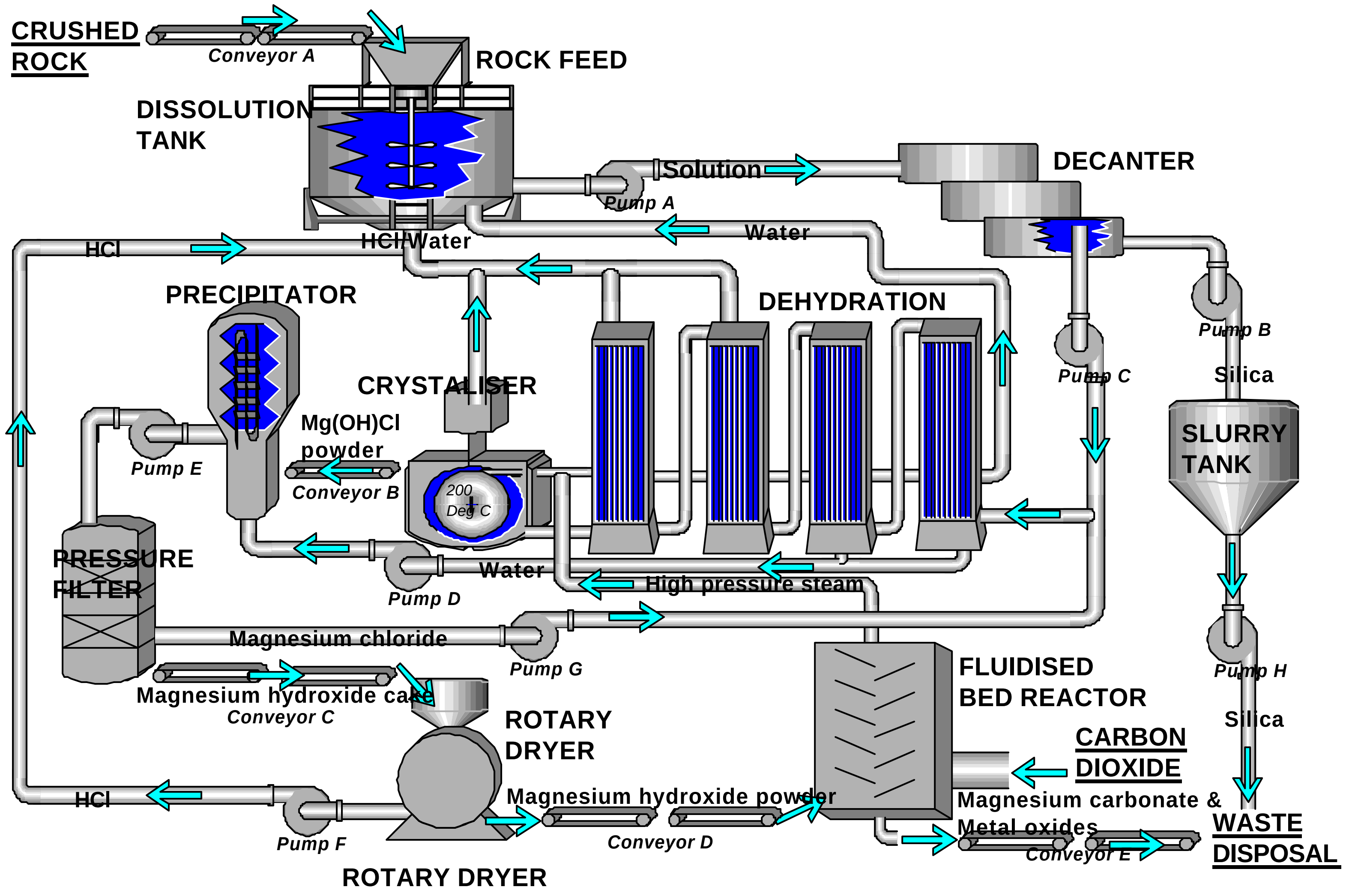
In order to provide an estimate for the actual cost of CO_2 sequestration, it is necessary to design a plant which is capable of meeting the demands of the process.

Such a plant is considered schematically in Figure 7.2, whilst a breakdown of the process in terms of equipment and flow mechanics is discussed below:

Dissolution Stage: The mined and crushed serpentinite is delivered to the plant and passes via a conveyor belt to the dissolution tanks. This is a stirred, insulated tank into which water and hydrochloric acid are recycled from downstream processes. The dissolution reaction occurs at a temperature of 80°C. A 15 minute reaction time has been assumed, and a glass lined reaction vessel has been used in the calculations.

Decantation Stage: The slurry from the dissolution stage is pumped to seven 30 m diameter thickeners used for counter-current decantation (CCD) washing. The objective is to remove the silica residue as a slurry from this series of thickeners. It is estimated that an underflow from the final thickener may be as high as 50% solids, and a solution loss has been computed on this basis. A more accurate estimate of potential losses would result from some laboratory test work on the products of dissolution. This would also confirm the choice of dewatering

Figure 7.2: Simplified Schematic of Method 1 Process



stage that would be most applicable for this material. CCD washing was assumed since this is the method used in the treatment of red mud residues in the Bayer process. The silica slurry is then pumped to the tailings dam for disposal.

Dehydration Stage: The overflow from the final thickener combines with the recirculated magnesium chloride filtrate to form the feed solution to the dehydration stage, where the removal of water and hydrochloric acid for use in other areas of the flow sheet is the objective.

This solution is pumped through the multiple effect evaporators where the water driven off in the first effects is used in the precipitators in a subsequent stage of the process, and the water/hydrochloric acid driven off in the final effects is returned to the dissolution stage.

A very crude estimate of the heat transfer surface area required has been made based upon a similar duty for sodium hydroxide liquors. The production of the MgOHCl powder is shown to require a further stage of dehydration in the form of a crystalliser. The costings have been calculated based entirely on the use of multiple effect evaporators. The actual plant selection will depend on the material and will require some laboratory analysis to confirm the most appropriate route.

Precipitation Stage: The MgOHCl powder is conveyed into the precipitators, which produce a magnesium hydroxide precipitate by mixing the powder in water, which comes from the evaporation stage. A unit size, based upon the available literature, has been taken as 250 m^3. It is estimated that 4 units of this size would be required. The materials for construction would need careful consideration and may well affect the costing further if exotic materials are deemed necessary (this would need to be considered once more information was available on the nature of the materials being handled). The slurry produced from these tanks is then pumped to the pressure filters.

Pressure Filtration Stage and Drying: The slurry from the precipitators is filtered under pressure to recover the magnesium chloride solution, which is recirculated to the dehydration stage. The filter cake consists of the magnesium hydroxide and some remaining saturated magnesium chloride solution. The degree of separation that can be achieved by the filtration stage can only be determined by test work, and so a value of 100 $kg/m^2/hr$ has been used for design purposes to estimate the filtration area required. A cake of 80% solids has been estimated in order to allow for losses of the magnesium chloride solution at this stage. This loss, together with the loss in the decantation stage, has been taken into account by an increase in the tonnage of rock required in the feed.

The filter cake is then conveyed to a rotary dryer, which serves the dual purpose of drying the cake and also breaking up the cake to produce the powder required for the final stage of the process. There will be a small tonnage of hydrochloric acid driven off in the dryer, which will be returned to the dissolution tank. The choice of filtration/drying combination that would be appropriate for this feed material cannot be established from the information that is available, once again laboratory tests would be required to allow this selection to be made. The units costed are thus selected in order to give a cost estimate, and are based on “similar” types of materials, and can thus only be used for guidance purposes.

Carbonation Stage: The dry magnesium powder is conveyed to the fluidised bed reactors. There will be several of these units in series, with the removal of CO_2 being performed on a cycle of progressive carbonation of the units in the sequence. An efficiency of 80% has been assumed for the utilisation of the magnesium hydroxide powder, and the feed rock tonnage has been increased to allow for this and ensure that all of the CO_2 is sequestered. Steam at high temperature and under pressure will be generated during this stage that can be utilised in the dehydration stage.

Although this stage has been costed on the basis that three 250 m^3 units would be required, it may be more appropriate to use more smaller units for the process. Also the pressure has been assumed to be 100 bar in these units, i.e. the pressure that the CO_2 will be delivered. The costings are for commercially available 60 bar units, thus a pressure reduction stage may need to be incorporated in the process. The magnesium carbonate and metal oxides are conveyed to the tailings disposal area.

7.5 Mass Balances

From the conceptual design of the plant, it is evident that a number of losses and inefficiencies within the process will necessitate an increase in the amount of serpentinite feed required to accommodate the target of 350 t per hour of CO_2.

As an illustration, the theoretical mass balance for the process, described in kg/s and t/hr, is shown in Figure 7.3, whilst the practical balance is shown in Figure 7.4.

The required rate of sequestration of 3Mt CO_2 per year requires theoretical input of 254.39 kg/s (915.8 t/hr) of magnesium silicate rock, on a 24 hours, 365 days a year basis. This produces sufficient magnesium hydroxide to react with 97.22 kg/s (350 t/hr CO_2 – producing 186.25 kg/s (670.5 t/hr) of magnesium carbonate.

Other waste and bi-products products include 104.33 kg/s (375.6 t/hr) of silica and 186.25 kg/s (90.1 t/hr) of metal oxides.

However, losses within the process, notably during the decantation and filtration stages require an increased rock input of 413 kg/s (1487 t/hr). The quantities of metal oxides and silica wastes are similarly increased. Process losses also indicate the need for 63.3 kg/s (228 t/hr) make-up HCl.

These inefficiencies and losses add to the general shortcomings of the process and exacerbate the huge energy input required for the principal evaporation stage.

Figure 7.3: Theoretical Mass Balance Method 1 in kg/s and *t/hr*

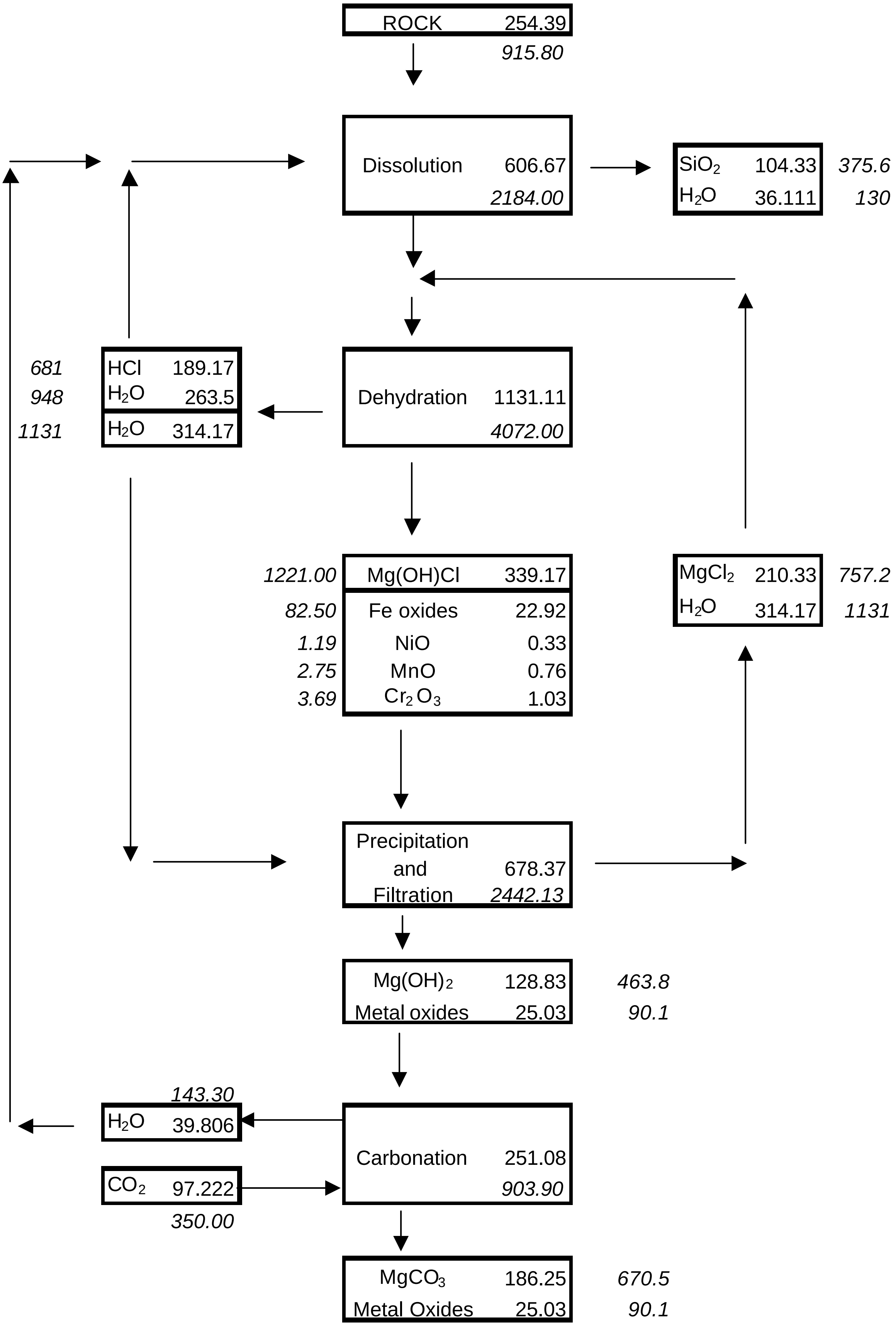
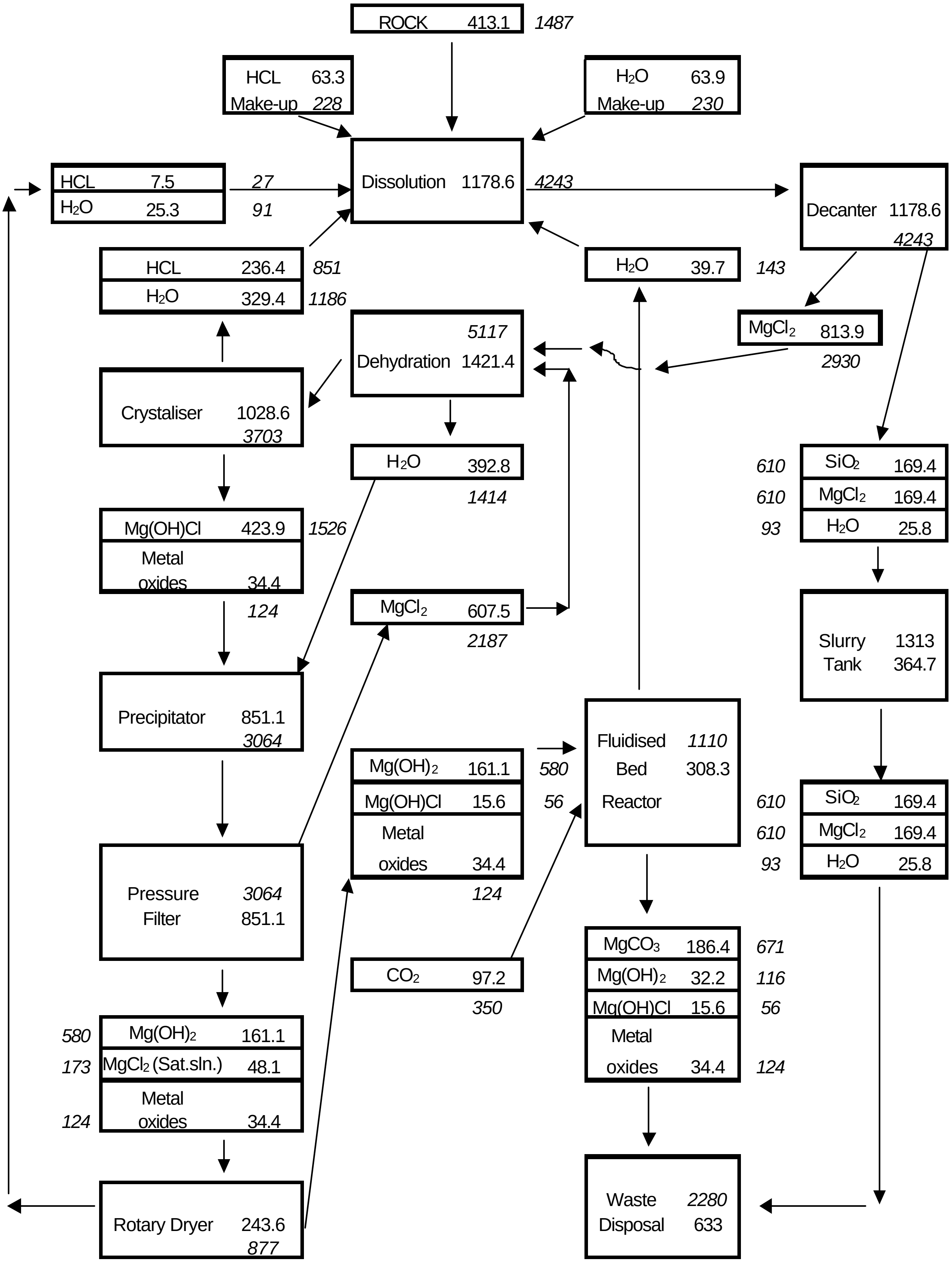


Figure 7.4: Practical Mass Balance Method 1 in kg/s and *t/hr*



7.6 Energy Balances

The energy requirements and generation for Method 1, based upon the processing of 1500 t/hr of serpentinite rock and 350 t/hr CO_2, are presented in Figure 7.5 and Table 7.9. Figure 7.5 shows the energy based on the enthalpy of reactions involved, whilst Table 7.9 presents the energy balance taking into consideration the practicalities of the process.

The enthalpy of reactions (Figure 7.5) would indicate a substantial generation of energy, with 3598 MW being released while 2304 MW are consumed. However, the practicalities of the process reverse this situation. A more realistic scenario is presented in Table 7.9. Here, most of the generated energy, from exothermic reactions, condensing water vapour and reforming HCl, is available only as low grade heat. Where this heat can be used, this has been incorporated into the process, but the bulk will go to waste and is unavailable for the major energy hungry processes of dehydration and drying.

The net result of the energy balance is calculated to be an overall requirement for 2204 MW for Method 1.

In more detail, the dissolution of the rock in HCl is approximately energy neutral, some of the excess heat from the dehydration stage being used to heat the solution to 80^oC. The dehydration and crystallisation stages together require 2131 MW. The precipitation stage is exothermic, releasing 301 MW, but in a form unavailable for the evaporation process. Drying of the filtrate requires a further 73 MW.

The carbonation stage is essentially energy neutral in that the enthalpy of carbonation is approximately equal to the heat required to heat the CO_2 and the magnesium hydroxide.

Only if substantial efficiencies can be made to the evaporation stage could this process begin to approach overall efficiency.

7.7 CO_2 Balance

The quarrying, comminution, chemical processing, ultimate site restoration and various ancillary activities incorporated in the sequestration of CO_2 involve a range of energy uses which can be considered as net generators of carbon dioxide. The CO_2 contribution from waste disposal/restoration is unknown, but for the purposes of this report will be considered comparable to quarrying, less the energy costs related to blasting and rock comminution.

A detailed CO_2 balance for the quarrying, comminution, processing and the waste disposal/restoration of the site in respect of Method 1 is shown in Table 7.10, whilst a CO_2 summary appears in Table 7.11.

The overiding impression form the CO_2 Balance is of a huge imbalance between CO_2 produced in comparison with that sequestered. The balance indicates a CO_2 production of almost 14 Mtpa compared with 3 Mtpa CO_2 sequestered.

Figure 7.5: Process Energy Requirements and Generation for Method 1 (1500 t/hr rock)

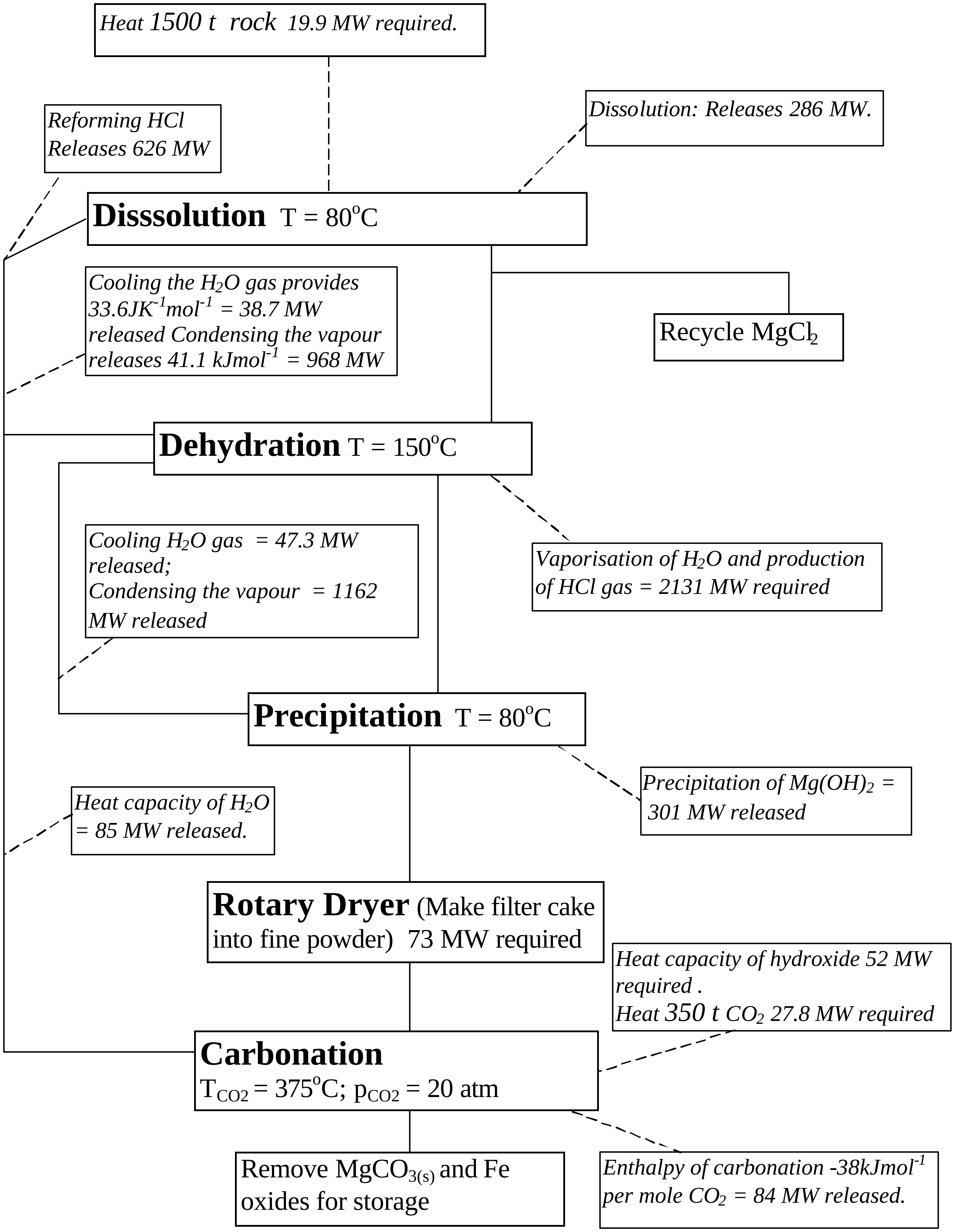


Table 7.9: Energy Balance Method 1 (MW)

	GAINS	LOSSES
Dissolution		
Approx. energy neutral	0	0
SUB TOTAL	0	0

Dehydration		
Evaporation of:		
H_2O re.crystaliser		-751
HCl re.crystaliser		-485
H_2O for precipitator		-895
SUB TOTAL	0	-2131

Precipitation		
Exothermic but insufficient for evaporation use	(301)	
SUB TOTAL	(301)	0

Rotary dryer		
Dehydration of:		
H_2O		-58
HCl		-15
SUB TOTAL	0	-73

Carbonation		
Enthalpy of carbonation	84	
Heat capacity of hydroxide		-52
Heat CO_2		-28
Approx. losses		-4
SUB TOTAL	84	-84

TOTAL	84	-2288

NET TOTAL	**-2204 MW**

A. Considerable amounts of energy are released in the cooling and condensation of vapours and steam produced during the dehydration/crystallisation stages. However, this is largely unavailable for processing purposes.

B. Energy use in quarrying and comminution of rock and waste disposal/restoration is minimal in comparison with the energy requirement for processing.

This is illustrated in the Carbon Dioxide Balance (Summary) Table 7.10.

Table 7.10: Carbon Dioxide Balance for Method 1 for 13 Mtpa

Processing							
	Units	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Dissolution stage reactors	30	20	600	5256000	5256	4362	A
Thickeners	7	214.3	1500	13140876	13140.876	10907	A
Evaporator electrical consumption	28	5	140	1226400	1226	1018	A
Precipitation reactors	4	170	680	5956800	5957	4944	A
Vacuum filtration	58	60	3480	30484800	30485	25302	A
Rotary Dryers	39	75	2925	25623000	25623	21267	A
Carbonation reactors	3	0	0	0	0	0	A
Conveyors	5	240	1200	10512000	10512	8725	A
Pumps	16	317	5072	44430720	44431	36877	A
General plant and office use	1	250	250	2190000	2190	1818	A
		Power MW			**Annual MWh**	**CO_2 t Annual**	
H2O Evaporation		2131			18667560	13067292	B
Rotary Dryers		73			639480	447636	B
Plant (As steel/t)	**Initial**	**Over process life**	**CO2/t equiv**	**CO2/t equiv annual**	**Factor re: design, manuf. etc**	**CO_2 t Annual**	
	100000	100000	230000	9200	10	92000	C
Quarrying, Crushing, Grinding etc							
	Quantity	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Quarry, electrical usage		615	615	5387400	5387	4472	A
					Carbon t		
Diesel Fuel tpa	5120				4000	14,680	
ANFO (explosive) tpa	3060				151	554	
	Rock t/hr	**kW**		**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Comminution	1500	23175		203013000	203,013	168,501	A
	Initial	**Quarry life**	**CO_2 t equiv**	**CO_2 t equiv annual**	**Factor re:**	**CO_2 t Annual**	
Plant (As steel/t)					**design, manuf. etc**		
	1000	2500	5750	230	10	2300	D
Waste Disposal/Resoration							
	Quantity	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Electrical usage, pumps etc.		615	615	5387400	5387	4472	A, E
					Carbon t		
Diesel Fuel tpa	5120				4000	14,680	E
Plant (As steel/t)	**Initial**	**Project life**	**CO_2 t equiv**	**CO_2 t equiv annual**	**Factor re:**	**CO_2 t Annual**	
					design, manuf. etc		
	1000	2500	5750	230	10	2300	D, E
TOTAL CO_2 Production (t/yr)						**13,934,107**	

A. At 0.83 t CO_2 per MWh sent out (P Freund, IEA, pers comm 1999). No correction for transmission inefficiency.

B. Evaporation of water and drying of product is achieved by oil heating. Figures are based upon Orimulsion carbon dioxide production of 0.7 tCO_2/MWh sent out.

C. New carbon steel production is equivalent to 2.3 t CO_2 per t steel. (P Freund, IEA pers. comm. 1999).
Factor x 10 for manufacturing, distribution etc.

D. New carbon steel production is equivalent to 2.3 t CO_2 per t steel.
Plant replacement = 2.5 x over 25 years and therefore 2500 x 2.3 = 5750t CO2 over 25 years. Factor x 10 for manufacturing, distribution etc.

E. Waste disposal activities are taken as comparable with quarrying, less comminution and blasting.

Table 7.11: Summary Carbon Dioxide Balance, Method 1

ROCK PRODUCTION		**CO_2 t Annual**
Quarrying	Electricity	4,472
	Diesel	14,680
	Explosives	554
Comminution	Electricity	168,501
Plant	Tonnes steel	2,300
	Sub Total	190,507
PROCESSING		**CO_2 t Annual**
Dissolution stage reactors	Electricity	4,362
Thickeners	Electricity	10,907
Evaporator electrical consumption	Electricity	1,018
Precipitation reactors	Electricity	4,944
Vacuum filtration	Electricity	25,302
Rotary Dryers	Electricity	21,267
Conveyors	Electricity	8,725
Pumps	Electricity	36,877
General plant and office use	Electricity	1,818
H_2O Evaporation	Diesel	13,067,292
Rotary Dryers	Diesel	447,636
Plant	Tonnes steel	92,000
	Sub Total	13,722,148
WASTE DISPOSAL/RESTORATION		**CO_2 t Annual**
Haulage	Diesel	14,680
Pumping etc	Electricity	4,472
Plant	Tonnes steel	2,300
	Sub Total	21,452

TOTAL	**13,934,107**

The principal producer of CO_2 is the dehydration/evaporation stage where there is an energy requirement of some 2131 MW, to be obtained from fuel oil, to remove water from the process fluid prior to the precipitation and filtration of magnesium hydroxide. The rotary drying of the filtrate requires approximately 73 MW. These two processes equate to a combined annual production of some 13.5 Mtpa of CO_2. In contrast, comminution of the rock material to <100 µm results in CO_2 production of 168,501 tpy from electrical consumption.

Preliminary consideration of the process plant operations suggests there is little opportunity to recycle heat from the dehydration and drying operations due to the low temperature of the waste heat.

These power hungry steps are absent from Method 3b where the general CO_2 balance appears, within the constraints of unknown kinetics, to be much more favourable.

7.8 Financial Appraisal

7.8.1 Introduction

Costs for financial evaluation of the two sequestration processes, Methods 1 and 3b are derived from the following sources:

- Current equipment prices;
- Industrial product prices converted to current values using the mean value from the US Bureau of Labour Statistics' Producer Price Index (Industrial Commodities) and (112 Construction Machinery and Equipment), and
- IEA Technical and Financial Assessment Criteria (Table 7.12).

Conversion of outdated price information to current value was undertaken according to the following formula:

$$\text{Cost at year (NOW)} = \text{Cost at year (THEN)} \times \frac{\text{Year (NOW) Cost Index}}{\text{Year (THEN) Cost Index}}$$

Prices obtained in £ sterling have been converted to US$ at the rate of £1 = US$ 1.60.

Basic plant prices have been increased by a factor of 2.1 to allow for the costs of such items as equipment erection, piping, instrument installation, process plant buildings, etc.

In addition, for this process, plant labour costs have been taken as the same as those for quarrying, and factorised for supervision and administration in accordance with the IEA Technical and Financial Assessment Criteria document.

IEA Technical and Financial Assessment Criteria makes provision for an allowance of 1% of installed plant costs for 'other chemical usage'. Theoretical mass balances for both Methods 1 and 3b indicate high degrees of recycling, however, process plant inefficiencies, particularly

Table 7.12: IEA Costing Criteria for Financial Analysis

PROJECT COSTS		**PROCESS OPERATIONAL COSTS**	
Predevelopment		Other chemicals $	1% of installed plant cost
Design		Maintenance (routine & breakdown):	
Procurement	2% of installed plant costs	SOLID PROCESSES	4% of installed plant cost
Project management		LIQUID PROCESSES	2% of installed plant cost
Permitting		Labour (operating)	Cost
Control systems	10% of installed plant cost	Supervision	20% of Labour (operating)
Land purchase	5% of installed plant cost	Overheads/admin	60% of Labour (operating)
		Insurances	1% p.a. of installed plant cost
EXTERNAL ECONOMICS		Contingencies	10% of installed plant cost
Loan/equity split	100% debt		
Interest rate	10%		
Discount rate/IRR	10%		
Loan period yrs	20		
Project lifetime yrs	25		
No inflation allowance	0		

associated with filtration and silica removal, necessitate substantial quantities of make-up chemicals. Method 1 requires inputs of hydrochloric acid whilst Method 3b needs additional magnesium chloride. Costs for these make-up chemicals are presented in the financial spreadsheets for both processes and add significantly to the cost per tonne of CO_2 sequestered.

7.8.2 Parameters

The spreadsheet calculations are largely parametric with parameters being derived from the IEA Technical and Financial Assessment Criteria document (Table 7.12) and standard commercial and financial criteria. The resulting spreadsheet for Method 1 (Table 7.13) requires explanation.

Plant lifetime has been assumed to be 25 years in accordance with the project brief, whilst the loan period has been set at 20 years. The other economic parameters shown in Table 7.12 were based upon IEA criteria and include predevelopment costs, land costs, control systems and the size of the contingency fund which were based upon percentages of the total installed plant cost.

Maintenance costs were based upon the nature of the processes involved, being 4% and 2% of the total installed plant costs for solid and liquid processes respectively. A standard diesel fuel cost of US$ 0.20/litre was taken to produce a derived cost of US$ 200/tonne. Electrical consumption was costed at US$ 0.05/kWh. The project brief required the sequestration of 350 t of CO_2 per hour, on a 24 hour, 365 days a year basis to meet the annual target of 3 Mt CO_2 sequestered. The Method 1 process requires the processing of 1500 t/hr of serpentinite rock in order to produce sufficient reactant to sequester the target load.

Financial data for operating labour for the mining/quarrying and comminution processes were based upon standard minerals industry costing methods, and have been costed at US $20/hr, utilising a four shift pattern giving 1940 hr/yr. This, and the supervision and overheads/administration costs, is in accordance with IEA criteria. Due to the innovative nature of the process, labour requirements for the process plant were taken as equivalent to those for the mining/quarrying and these numbers, as well as the staff distribution between different process operations, must be taken as an estimate.

There is a provision for the costs of ‘other chemicals’, of 1% of installed plant costs. This figure is substantially elevated for process stages 1, 3 and 4 (Table 7.13). In the case of stages 1 and 3, this is due to the inclusion of known and quantifiable chemical inputs including explosives and specialised grinding fluids. With regard to the elevated figure for process stage 4, this is a consequence of the substantial make-up input of hydrochloric acid to replace chloride lost through process inefficiencies (Figure 7.4). The HCl input is necessary at the dissolution stage and the costs for this acid have therefore been included in this stage.

With the exception of conveyors and pumps, process stages as shown in the spreadsheet (Table 7.13) are sequential, permitting a view of the escalation of costs with progress through

Table 7.13: Financial Spreadsheet for Method 1

Economic Parameters			Capital Parameters			Operations parameters		
Interest rate	10.0%		Predevelopment	2%	Installed plant	Fuel cost	200.00	$/t
Equity/Loan split	0.0%		Land cost	5%	Installed plant	Electricity cost	5.00	c/kWh
Plant lifetime	25	years	Control systems	10%	Installed plant	Other chemicals	1.0%	Installed plant
Loan period	20	years	Contingences	10%	Installed plant	Maintenance -solids	4.0%	Installed plant
Inflation rate	0.0%					Maintenance -liquids	2.0%	Installed plant
Rates	1.0%	Installed plant	Discount rate	5%	10%	CO_2 processed	350	t/h
Insurance	1.0%	Installed plant	Sequestration price ($/t)	230.78	233.06	Rock processed	1500	t/h

Process Stage	Description	Number of Units	Unit Costs	Installed Plant Cost	Predevelop Costs	Land Cost	Control Systems	Contingency Costs	Capital Cost	Fuel Consumption	Fuel Cost	Power Consumption	Electricity Cost
			($M)	($M)	($M)	($M)	($M)	($M)	($M)	(t/yr)	($M)	(kW)	($M)
1	Mining operations	1	27.521	27.52	0.55	1.38	2.75	2.75	**34.95**	5120	1.02	615	0.24
2	Communition - crushing	1	23.110	23.11	0.46	1.16	2.31	2.31	**29.35**	0	0.00	2250	0.99
3	Communition - grinding	1	38.800	38.80	0.78	1.94	3.88	3.88	**49.28**	0	0.00	20925	9.17
4	Dissolution reactors	30	0.289	8.67	0.17	0.43	0.87	0.87	**11.01**	0	0.00	600	0.26
5	Decanter/thickener	7	1.157	8.10	0.16	0.40	0.81	0.81	**10.29**	0	0.00	1500	0.66
6	Dehydration evaporators	28	0.821	22.99	0.46	1.15	2.30	2.30	**29.19**	1755341	351.07	0	0.00
7	Precipitation reactors	4	2.315	9.26	0.19	0.46	0.93	0.93	**11.76**	0	0.00	680	0.30
8	Pressure filters	58	3.360	194.88	3.90	9.74	19.49	19.49	**247.50**	0	0.00	3480	1.52
9	Rotary dryers	39	4.103	160.02	3.20	8.00	16.00	16.00	**203.22**	60131	12.03	2925	1.28
10	Carbonation reactors	3	2.315	6.95	0.14	0.35	0.69	0.69	**8.82**	0	0.00	0	0.00
11	Conveyors	5	0.084	0.42	0.01	0.02	0.04	0.04	**0.53**	0	0.00	1200	0.53
12	Pumps	16	0.166	2.66	0.05	0.13	0.27	0.27	**3.37**	0	0.00	5072	2.22
Total				**503.37**	**10.07**	**25.17**	**50.34**	**50.34**	**639.27**	**1820592**	**364.12**	**39246**	**17.16**

Table 7.13 (contd.):

Labour parameters		
Operating labour rate	20.00	$/h
No of shifts	4	
Operating time per shift	1940	h/yr
Supervision	20.0%	labour
Overheads & Admin	60.0%	labour

Process Stage	Other Chemicals ($M)	Operating Labour per Shift	Operating Labour Cost ($M)	Supervision Cost ($M)	Overhead Cost ($M)	Maintenance Cost - Solids ($M)	Maintenance Cost - Liquids ($M)	Annual Rates ($M)	Annual Costs ($M)
1	6.500	25	3.88	0.78	2.33	1.10	0.55	0.28	**16.67**
2	0.790	20	3.10	0.62	1.86	0.92	0.46	0.23	**8.98**
3	7.090	20	3.10	0.62	1.86	1.55	0.78	0.39	**24.56**
4	175.761	5	0.78	0.16	0.47	0.35	0.17	0.09	**178.03**
5	0.081	2	0.31	0.06	0.19	0.32	0.16	0.08	**1.86**
6	0.230	4	0.62	0.12	0.37	0.92	0.46	0.23	**354.02**
7	0.093	2	0.31	0.06	0.19	0.37	0.19	0.09	**1.60**
8	1.949	5	0.78	0.16	0.47	7.80	3.90	1.95	**18.51**
9	1.600	5	0.78	0.16	0.47	6.40	3.20	1.60	**27.51**
10	0.069	2	0.31	0.06	0.19	0.28	0.14	0.07	**1.11**
11	0.004	0	0.00	0.00	0.00	0.02	0.01	0.00	**0.56**
12	0.027	0	0.00	0.00	0.00	0.11	0.05	0.03	**2.43**
Total	**194.19**	**90**	**13.97**	**2.79**	**8.38**	**20.13**	**10.07**	**5.03**	**635.85**

Summary Data

Process Stage	Description	Capital Cost ($M)	Annual Costs ($M)
1	Mining operations	**34.95**	**16.67**
2	Communition - crushing	**29.35**	**8.98**
3	Communition - grinding	**49.28**	**24.56**
4	Dissolution reactors	**11.01**	**178.03**
5	Decanter/thickener	**10.29**	**1.86**
6	Dehydration evaporators	**29.19**	**354.02**
7	Precipitation reactors	**11.76**	**1.60**
8	Pressure filters	**247.50**	**18.51**
9	Rotary dryers	**203.22**	**27.51**
10	Carbonation reactors	**8.82**	**1.11**
11	Conveyors	**0.53**	**0.56**
12	Pumps	**3.37**	**2.43**
	Total	**639.27**	**635.85**

the entire process, and allowing assessment of the cost contribution generated by each stage of the process.

Total capital costs are shown to be approximately US $640M, to include the mining, comminution and sequestration process plant, but not including waste disposal capital costs. In view of the uncertainties regarding the form, composition and characteristics of this waste it may be assumed to generate similar capital and operating costs to the mining/quarrying operation. On this basis, waste disposal operations may be expected to add approximately a further US $6.85 t/$CO_2$ sequestered to the sequestration price shown in the spreadsheet.

Approximately a third of the total capital costs is accounted for by each of stages 8 and 9 (pressure filtration and rotary drying of the products prior to carbonation). The capital costs are based upon unit costs of commercially available units. It is possible economies may be gained from bulk purchase discounts or custom designed units, but these possibilities are beyond the scope of this study. Table 7.14 shows a more detailed cost breakdown for the process plant.

Total annual operating costs are shown to be approximately US $636M, almost equal to the capital costs. More than 50% of the operating cost is accounted for by the fuel requirement for the dehydration stage of the process. A further 15.5% is generated through the current world costs of making up HCl lost to the process. It is worth noting that the HCl make-up requirement represents a significant (0.33 – 0.5) fraction of the current world production.

Mining and quarrying costs comprise less than 3%, and comminution costs slightly more than 5% of the total operation annual costs.

Thus, the major costs are primarily associated with the process plant, and above-all, fuel and make-up chemicals. The final sequestration price of US $233.06/t CO_2 sequestered would require reduction by an order of magnitude before the process could be widely considered as economically viable in the current economic situation. Even allowing for error, the possibility of capital cost reductions as described, maximum automation and optimum sourcing of consumables, it remains difficult to see where such an overall reduction in costs can be achieved.

7.9 Bi-product Production

Serpentinite, the proposed feedstock for Methods 1 and 3b for CO_2 sequestration, typically contains approximately 10% metal oxides. Of this more than 90% is iron, with significant quantities of chromium, nickel and manganese. It is anticipated these will be expressed as oxides in the final waste products, in association with magnesium carbonate and silica.

For the scale of proposed operation of approximately 13 Mt (Method 1) or 8 Mt (Method 3b) of serpentinite per year for a single plant sequestering 3 Mt CO_2, then such a plant will produce significant tonnages of metals. If the process is extrapolated to assume that the target

Table 7.14: Method 1 Process Costs

Item	Units	Cost £	Total cost £	Total adjusted cost £	Total adjusted cost US $	Factorised costs US $	Unit cost US$
Dissolution Reactors	30	55000	1,650,000.00	2,583,275	4,133,240	8,679,805	289327
Decanter/thickener	7		1,540,000.00	2,411,057	3,857,691	8,101,151	1157307
Dehydration evaporators	28	156,000	4,368,000.00	6,838,634	10,941,815	22,977,811	820636
Precipitation reactors	4	440,000	1,760,000.00	2,755,494	4,408,790	9,258,459	2314615
Pressure filters	58	1,000,000	58,000,000.00	58,000,000	92,800,000	194,880,000	3360000
Rotary Dryer	39	780,000	30,420,000.00	47,626,202	76,201,923	160,024,039	4103180
Carbonation reactors	3	440,000	1,320,000.00	2,066,620	3,306,592	6,943,844	2314615
Conveyors	5	16,000	80,000.00	125,250	200,400	420,839	84168
Pumps	16	31,500	504,000.00	789,073	1,262,517	2,651,286	165705
					197,112,968	**413,937,233**	

Assume £1 = $1.60

Factors re. associated activity	
Equipment erection	0.45
Piping	0.45
Instrument installation	0.15
Electrical	0.1
Process buildings	0.1
Utilities	0.45
Storage facilities	0.2
Ancillary buildings	0.2
TOTAL	**2.1**

Installed plant cost US $	**413,937,233**
Other costs US$	**141,640,812**
TOTAL PROCESS COSTS	**555,578,045**

figure for 2025 of 1 Gt CO_2 per year must be sequestered, then the potential metal production is large enough to impact upon current mining practices.

To appreciate the levels of potential metal production from a 3Mt CO_2 per year plant and to consider the impact if the 1 Gt CO_2 per year target is met, Table 7.15 attempts to quantify the metal oxide outputs for each scenario.

Table 7.15: Metal Oxide Production From Serpentinite (Composition as per Table 7.2)

Production Rate 1487 t/hr (Method 1)					
Metal Oxide	%	kg/s	t/h	t/y	Mt/1GtCO_2/y
Fe_2O_3	2.5	10.3	37.1	324,869	108
FeO	6.5	26.8	96.4	844,652	281
MnO_2	0.13	0.54	1.9	16,890	6
Cr_2O_3	0.4	1.65	5.9	51,979	17
NiO	0.3	1.24	4.5	38,984	13
Total		**40.5**	**146**	**1,299,478**	**425**

Production Rate 916 t/hr (Method 3b)					
Metal Oxide	%	kg/s	t/h	t/y	Mt/1GtCO_2/y
Fe_2O_3	2.5	6.347	22.85	200,166	66.7
FeO	6.5	16.50	59.41	520,432	173.5
MnO_2	0.13	0.330	1.19	10,406	3.5
Cr_2O_3	0.4	1.016	3.66	32,026	10.7
NiO	0.3	0.762	2.74	24,019	8.0
Total		**24.955**	**89.85**	**787,049**	**262.4**

These metals will be present as a potential waste material for disposal. If it is possible to economically separate them from the waste stream then there is the potential to generate a substantial cash-flow, to a maximum, at recent prices, of approximately $132,000,000 per year (Table 7.16).

Table 7.16 Potential value of metal ores resulting from 3Mt CO_2 sequestration.

1487 t/hr (Method 1)				
June 1998 Prices	US $/t (mean)	t/h	US $/h	US$M/year
$Fe_2O_3^*$	21	37.1	779	6.8
FeO^*	23.34	96.4	2,250	19.7
MnO_2	195	1.9	371	3.2
Cr_2O_3	65	5.9	384	3.4
NiO^+	2,500	4.5	11,250	98.6
Total		**146**	**15,034**	**131.7**

916 t/hr (Method 3b)				
Fe_2O_3[*]	21	22.85	479.85	4.2
FeO[*]	23.34	60.96	1422.9	12.5
MnO_2	195	1.19	231.66	2.0
Cr_2O_3	65	3.66	237.64	2.1
NiO[+]	2,500	2.74	6,850	60.0
Total		**91.40**	**2372.05**	**80.8**

[*] Iron ore price based on 30 US cent/t for each percentage point Fe content. Thus, FeO = 77.78% Fe and Fe_2O_3 = 70% Fe.

[+] Price estimate based on approximately half the current LME metal price.

The potential inputs of chromium, nickel and manganese could have a significant impact upon current world metal prices and mining operations. If metals were to be produced in the amounts shown above, then it is beyond doubt that prices would fall significantly from their current levels, thus creating serious implications for many traditional mining areas of the world where iron, nickel and chromium are produced.

Similarly, magnesite (magnesium carbonate), currently sells at $120/t, although world production is relatively modest, being an order of magnitude less than the 5,869,000 t per year production from a single 3 Mt CO_2 processing plant. Clearly, if a beneficial use can be established for the magnesite, then there is the potential for a significant reduction in overall process costs. In reality, the enormous tonnages of magnesite anticipated to be produced would dwarf the demand needs of any existing or new use, thus precluding any opportunity to generate revenue from this part of the waste stream.

7.10 Rehabilitation and Restoration

7.10.1 Degree of Clean-up

One of the guiding principles of policy regarding modern world-wide mineral workings is that of site restoration. Historically, many quarry and mine sites have been abandoned in an unacceptable and dangerous condition. Today, many nations still require adequate site restoration and restoration funding commitments as a prerequisite of planning permissions, extraction licences or other permitting procedures.

However, the costs and extent of site restoration and remediation will vary depending upon the marginal value of the land and the proposed end use. Where an industrial site has been developed on a virgin site, then restoration costs will be high if the object of restoration is to restore to the pre-development condition. If the site is to be restored for other industrial use, then costs will be greatly reduced.

Given the “environmental” nature of the project as a whole, it is likely that environmentally sound restoration will be required from the quarry operators. The proposed CO_2 sequestration facility would include three distinct areas requiring restoration – the processing plant, the quarry and the tailings pond.

7.10.2 Remediation Costs

Remedial costs are highly site specific (USA EPA, 1997), and future costs may be significant especially where the long term performance of a remedial alternative/mitigation measure cannot be accurately predicted and/or where perpetual care is likely to be needed.

In an attempt to estimate remediation costs in relation to surface mining of coal in the USA, costs were found to vary by a factor of 10 between sites and reclamation costs had a similar impact on the price per tonne of product. After the introduction of the Surface Mining and Reclamation Act (USA 1975), the President's Commission on Coal found the increase in reclamation costs would range from $0.10 to $17.77 per tonne of coal produced (Wiener 1980). In trying to draw conclusions regarding rehabilitation costs Weiner stated "comparisons are difficult, if not impossible". This is due largely to varying site specific features, local and, by inference, national legal requirements.

For the purposes of this study, the costs of remediation and site rehabilitation are taken as equivalent to 10% of the process plant capital costs and 10% of the tailings dam operating costs. It is assumed the quarry is left as a void. Process plant costs of $600 million and tailings/waste management costs over the 25 year project life of $138.6 million lead to an estimated restoration/rehabilitation cost of $73.9 million - $2.95 million per year or 98c per tonne of CO_2 sequestered.

Costs of on-going waste disposal and management throughout the life of the project are taken as equivalent to the mining and quarrying costs (Table 7.13) which equates to US $6.85 t/$CO_2$ sequestered.

7.10.3 Process Plant Decommissioning

The main components of the process plant may be expected to be steel and other metal alloys for processing tanks, vats etc; concrete from buildings and foundations; plastics from construction and processing equipment and mixed component electrical equipment.

None of the processes involved in CO_2 sequestration generate or use particularly hazardous materials and there is no reason to assume that there will be any undue contamination of the construction materials.

There may be some contamination from accidental spillage of materials such as diesel fuel which may be anticipated during the proposed 25 year life of the plant, but appropriate design and management of storage and handling areas, as well as the main process plant, should minimise this hazard.

In comparison with such projects as nuclear power generation, oil processing, metal mining or production of many organic and agro-chemicals, the process plant itself poses few problems for ultimate remediation and restoration of the site.

The cost of plant decommissioning hinges upon a number of factors:

- Degree of clean-up required;
- The nature and scale of the plant;
- The nature and scale of the plant activities;
- The nature and scale of any post closure residual material;
- The type, volume and degree of contamination of the plant;
- The nature of any hazards associated with plant contamination;
- Recyclability/re-use of the plant materials, and
- Site specific elements including those related to geography, access, urgency and public demand.

However, the overall degree of restoration will depend on public and state requirements.

7.10.4 Open Pit

It is assumed that the completed open pit will be left as a void, or allowed to fill with water as the water table rebounds. Most major quarries are subject to inflows of water and operating costs will accrue during production.

The amount of water involved is directly related to the nature of the rock and the height of the water table. Serpentinite has a low intrinsic permeability, but is often heavily fractured. Thus, while it rarely holds substantial quantities of water, it may provide routes allowing water into the quarry. However, although requiring pumping, it is feasible that the water would be of sufficient quality to be used for agricultural irrigation, or release directly to the surface drainage.

For the purposes of this study pumping costs are included in the overall mining cost, whilst costs of water treatment are considered in the remediation costs given above.

7.10.5 Hydrocarbons

A major cause of contamination within quarries is the leakage of various hydrocarbons such as fuels, hydraulic oils, etc, from plant, vehicles and storage tanks. As a matter of policy, all contaminative materials should be stored in bunded areas with the capacity to safely contain 120% of maximum stored capacity. Similar storage protection should be made for solvents, acids, alkalis, bulk fuel oils, etc.

Hydrocarbon contamination of groundwaters is of increasing concern and very costly to remediate. A minor oil spill at Paradise Peak Mine, FMC Gold, Nevada, with little potential for ground or surface water impacts, generated costs of over $100,000 for preventative works, soil removal, etc (US EPA 1997).

An effectively implemented environmental management system will greatly reduce the risk of accidental contaminative incidents.

7.10.6 Coarse Tailings

During production, quarry material will be generated which is not suitable for processing as feedstock to the sequestration plant. Initially this material will require surface storage. However, the extent of these surface deposits should be minimal with respect to the overall extent of the quarry.

Appropriate choice and management of the spoil storage site can effectively avoid the need for costly restorative measures. Care is needed to avoid precipitation run-off and other surface water impacts. Once the quarrying has progressed to the point where restoration can begin, then spoil can be placed as backfill.

7.10.7 Tailings dam

The final product of the sequestration process will be a combination of silica (SiO_2), magnesium carbonate ($MgCO_3$) and, unless they can be economically removed as ores, a substantial tonnage of metals, notably iron, nickel, chromium and manganese. It is anticipated these metals will occur primarily as oxides, which generally exhibit considerable stability. However, until trial work is completed, the precise nature of the metals and their potential mobility will not be known.

Although a sizeable void will be created during the mining of the source material, practical difficulties of combining back fill into a working quarry, combined with the nature of the fill material, demand that the bulk of the waste be deposited in a tailings dam.

The costs for the restoration of tailings dams relate primarily to:

- Size;
- The chemical and physical form of the fill;
- The extent and nature of any human or other environmental hazard presented by the fill material itself;
- The long term safety and stability of the dam;
- The extent and hazard presented by hydrological effects due to seepage from the dam;
- Degree of restoration required by initial permitting, and
- Availability of appropriate capping, landscaping and replanting material.

The composition of the tailings appears to pose little direct hazard, other than that associated with windblown dusts. Sufficient experience exists to ensure the long term safety of the dam structure.

Appropriate engineering and management of tailings dams can be critical to the operational success of mining projects. Major pollution incidents resulting from failure of metal mining tailings dams may entail many millions of dollars in remediation costs and damages (US EPA 1997).

7.10.8 Fill Stabilisation and Compaction

The physical and chemical form of the carbonate end product is not currently known. It is anticipated that the carbonate material for disposal will be in the form of a powder, with a grain size < 10 µm. If the material is well graded, then stability problems may occur as grains effectively roll against each other. However, it is likely that the carbonate may be stored together with the silica "gel" and other bi-products within a single tailings impoundment, although the long-term storage implications are not fully understood.

7.10.9 Top Soil

Any top soil or sub-soil with potential as a medium for use in restoration and rehabilitation should be saved from quarry surface stripping, plant construction operations and the building of the tailings dam.

Ultimate restoration of tailings dams typically requires capping with inert material, sub-soil and top-soil. Any efforts to generate or maintain supplies of these materials on site will reduce the eventual costs or restoration by avoiding or minimising the need to import capping material.

The restoration value of top soil can rapidly decline if stored inappropriately. Optimal quarrying sites tend to exhibit thin top and sub soils, and thus it is unlikely that, if progressive restoration is carried out, storage areas for top soil and sub-soil need be greater than 10% of the extent of the quarry. If progressive restoration proves impractical then it may be necessary to allocate substantial storage areas if the quality of the top soil is to be maintained.

7.11 Conclusions

At the outset of this project, the previous work undertaken on the subject of mineral carbonate sequestration had indicated that an acid dissolution route utilising an ultramafic feed to produce the stable mineral carbonate may provide an acceptable method for CO_2 storage.

The thermodynamics of the process appeared favourable, as did the kinetics for the main carbonation reaction. However, what the early work did not consider were the implications for industrial scale-up of the process and the problems which this creates.

On a positive note, the scaling of the plant to accommodate the 3Mtpa CO_2 requirement presents few real problems with regard to mining, primary processing and final waste disposal/storage, as the tonnages involved are well within the production levels experienced by many mining operations around the world.

Similarly, the geometry, equipment and logistics of the proposed plant design are not thought to present major problems in construction.

However, the main process of sequestering the CO_2 has a fundamental drawback in that most of the generated energy, from exothermic reactions, condensing water vapour and reforming HCl, is available only as low grade heat. Where this heat can be used, this has been incorporated into the process, but the bulk will go to waste and is unavailable for the major energy hungry processes of dehydration and drying.

This has resulted in the requirement of enormous amounts of energy for the dehydration and crystallisation stages which in practical terms equates to a requirement of more than four times the amount of energy produced by the 500 MW power station for which the process has been designed to accommodate. This translates to a process producing more CO_2 than it sequesters.

This factor alone, using the current parameters, renders the process non-viable.

In addition, due to the overall inefficiencies and losses of the process, make-up HCl is required to constantly replenish the reactants for the dissolution stage. For the proposed method, this extra acid represents nearly a third of annual world production. Acquiring this volume of acid is not a realistic proposition.

Taken together, these two critical factors, when combined with the other costs associated with the process route, escalate the sequestration cost to US $233 per tonne of CO_2 (at a 10% discount rate). This is a factor of ten greater than would be necessary to stimulate current interest in the process.

As a final note, although the discussion above has highlighted the shortcomings of the process, it was originally hoped that the value of a number of important bi-products such as iron, manganese, chromium and nickel, may provide some revenue from the process.

Although the value of these commodities at current prices is high, production of these metals from the sequestration process at the levels anticipated would swamp the world markets for these metals, automatically sending prices downwards. What levels these prices may stabilise at, and whether there would be a market for such enormous tonnages, are beyond the scope of this project, although if a more efficient sequestration method could be found, then bi-product revenue may have a part to play in the equation.

8.0 DIRECT CARBONATION OF THE MELT – AN ALTERNATIVE APPROACH

8.1 Introduction

The alternative approach recently suggested by Wendt et al (1998) which involves the direct carbonation of the dissolved silicate in a melt of $MgCl_2$ has the major advantage that it avoids the highly energy intensive dehydration and crystallisation steps which effectively prohibits the commercial development of Method 1.

This Method 3b has been described briefly in Section 5 where the thermodynamics, magnitude of the process and technological level of the plant all appear to be favourable towards industrial scale sequestration. However, as has already been stated, the kinetics of this process are unproven and thus it is only possible to present a “what if?” scenario for the purposes of this report whereby reaction and residence times have been selected based on comparable industry processes.

As detailed in Section 7, the source of raw materials, extraction methodology and primary processing have already been discussed, as the basic process utilises a serpentinite feed at an hourly rate of 916 t to give an annual production of approximately 8 Mt. However, all other aspects of the process are different to Method 1 and are presented below.

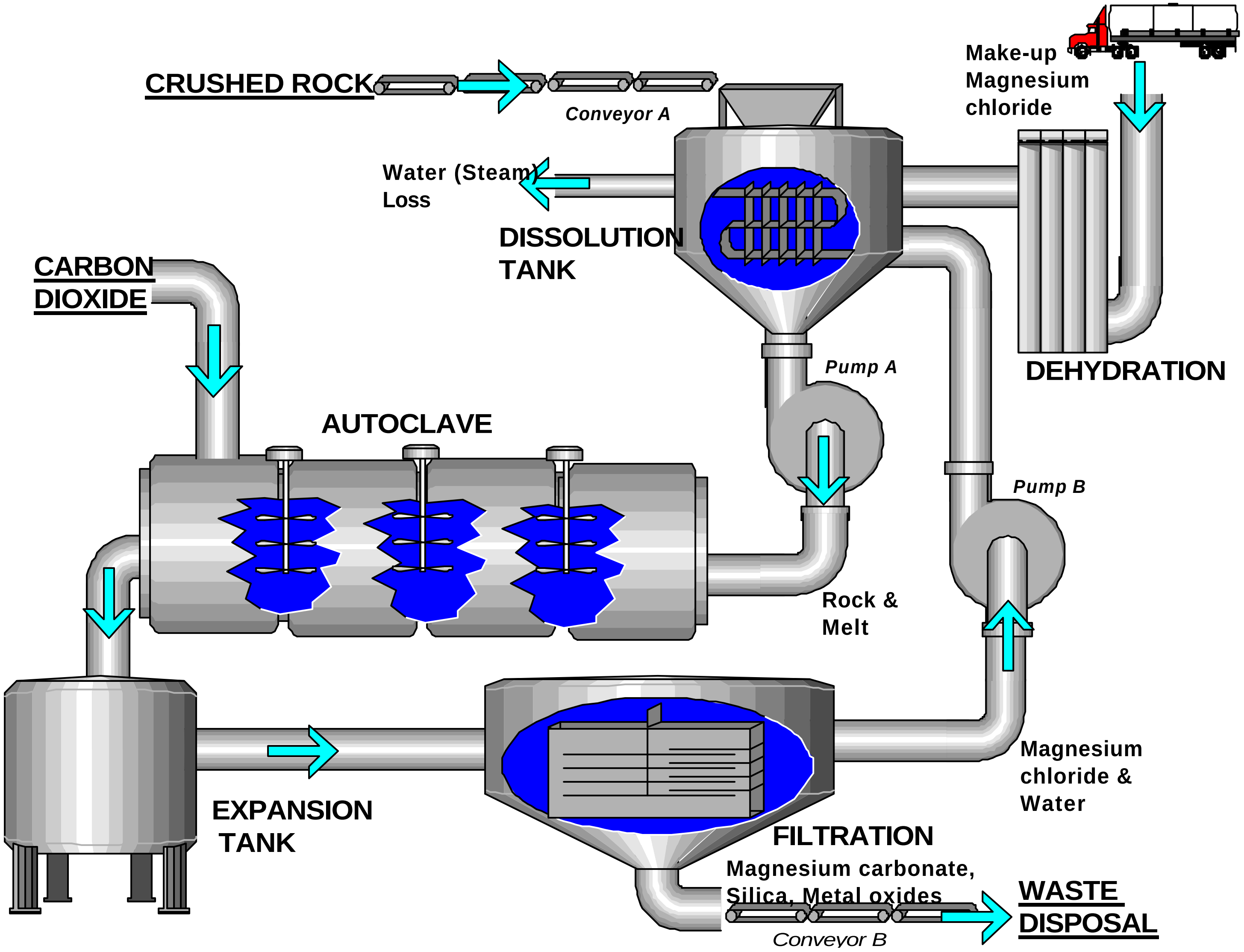
8.2 Process Plant

The proposed flowsheet for Method 3b (Figure 8.1) is considerably simplified in comparison to that put forward for Method 1. In basic terms, there are three main process stages:

Mixing Stage: The mined and crushed serpentinite is delivered to the plant and passes via a conveyor belt to the feed hopper for the mixing tanks. This is a stirred, insulated tank into which the magnesium chloride melt (recycled from downstream processes) and make-up magnesium chloride and rock are added. A 15 minute residence time has been assumed for this stage. This process will be controlled at 250°C and 2.7 bar, thus, any excess water contained in the melt will be removed by control of the pressure and a bleed system, whilst energy input will be required to drive off the water. The rock will dissolve in the melt and the solution will be pumped to the next stage.

Sequestration Stage: The solution is pumped into autoclaves operating at 30 bar pressure and 300°C, into which the CO_2 is delivered. One hour has been allowed for this reaction to take place. An autoclave size of 250 m^3 has been used in the calculations (autoclaves of this size and operating under the conditions of temperature and pressure required here, are in use in the gold industry). A refractory lined, agitated vessel will be required. The products of reaction (magnesium carbonate, silica and metal oxides) are removed in the filtration stage that follows.

Figure 8.1: Simplified Schematic of Method 3b Process



Pressure Filtration Stage: The slurry from the autoclaves is filtered under pressure to recover the magnesium chloride melt, which is recirculated to the dehydration stage at 250°C and 2.7 bar. An expansion tank has been included in the flowsheet to allow for a reduction in pressure from the 30 bar of the autoclave to the operating pressure of the filters. The filter cake consists of the magnesium carbonate and some remaining magnesium chloride melt. The degree of separation that can be achieved by the filtration stage can only be determined by test work, and so a value of 100 kg/m^2/hr has been used for design purposes to estimate the filtration area required. A cake of 80% solids has been estimated in order to allow for losses of the magnesium chloride melt at this stage. This has been taken into account by a make-up stream of magnesium chloride in the mixing tanks. The filter cake is then conveyed to the disposal system.

8.3 Mass Balance

The basic mass balance for Method 3b uses the same rock input as the theoretical input and final output figures for Method 1 (Figure 8.2). However, it can be seen that the elimination of separate dehydration, precipitation and filtration stages prior to carbonation significantly reduces mass flows through the process plant.

A proportion of the melt utilised in Method 3b will be lost in the filtration stage. It is estimated that there will be a magnesium chloride make-up requirement of 36.7 kg/s (132 t/hr), which is equivalent to approximately 2.5% of the total mass of the melt (1400 kg/s, 5042 t/hr). This could be supplied as the bought-in manufactured chemical at a cost of approximately £70 (US $112) per tonne – or £80,940,000 (US $129,507,840) per year. However, this would require a significant fraction of current world production. Also the energy/CO_2 balance for industrial $MgCl_2$ production while not investigated within this report may well be significant. Figure 8.3 shows the practical mass balance including the contribution from the $MgCl_2$ make-up.

An alternative is the generation of $MgCl_2$ from the dissolution of additional magnesium silicate rocks in hydrochloric acid in a similar process to that required for the preliminary stage of Method 1. This method will produce a $MgCl_2$ hydrate which requires partial evaporation. This can be anticipated to have a significant impact on the overall energy requirement/carbon balance for Method 3b and should be derived to permit a more precise evaluation of the energy/carbon dioxide “costs” of this approach.

A simplified schematic of Method 3b including the magnesium chloride make-up process plant is shown in Figure 8.4. Here the production of 132 t/hr of $MgCl_2$ requires the dissolution of 116 tonnes or rock in 86 tonnes HCl and 147 tonnes of water. The rock solution is pumped to a smaller but similar decantation system as that used in Method 1 for the removal of waste silica. The bulk of the solution is then subject to partial evaporation, requiring 37 MW, to produce $MgCl_2$ in the same composition as the active melt in Method 3b. Approximately 40% of the input water is returned from the evaporation stage for reuse. A detailed mass balance for this make-up phase is shown in Figure 8.5.

Figure 8.2: Theoretical Mass Balance for Method 3b in Kg/s and *t/hr*

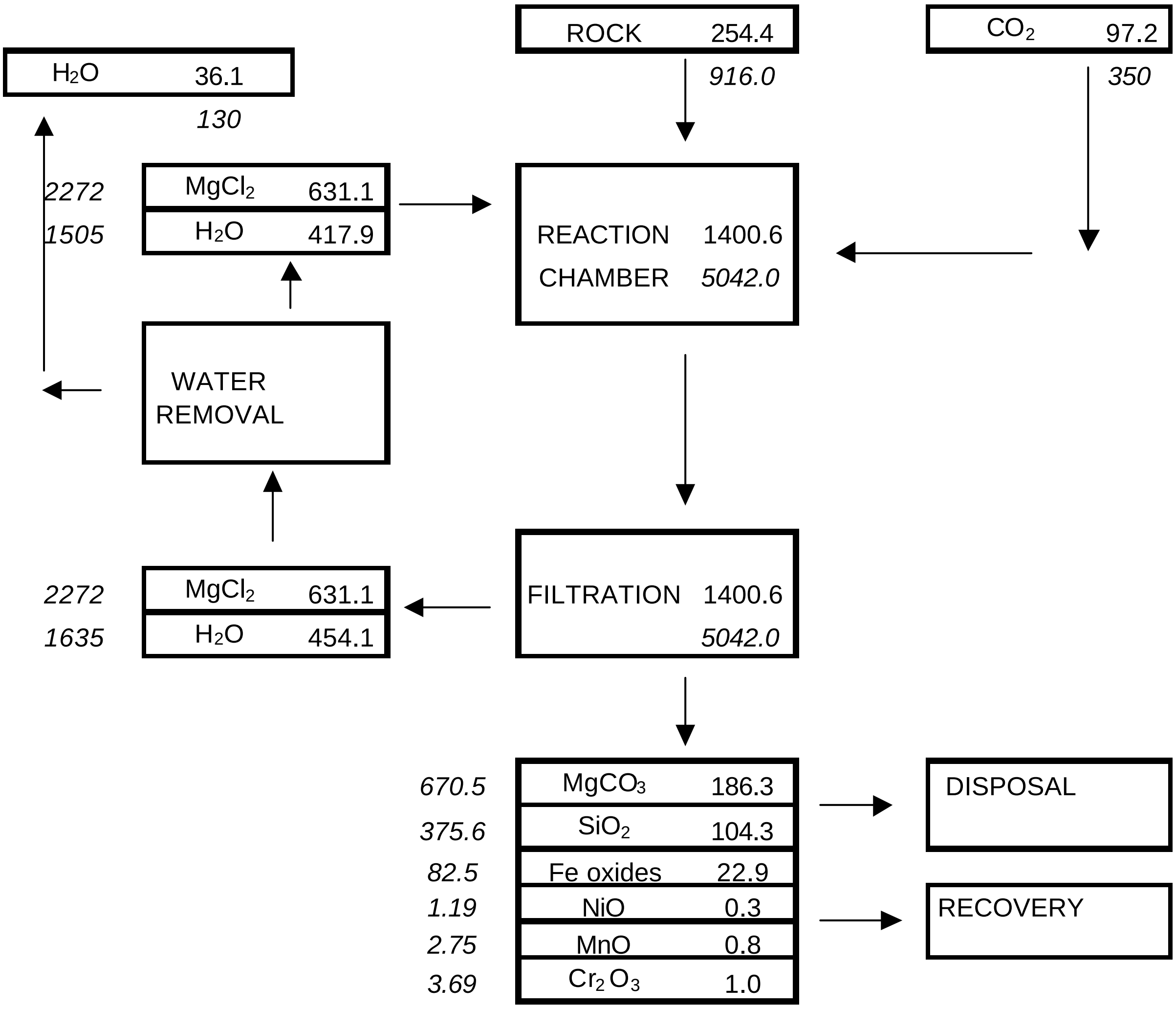


Figure 8.3: Practical Mass Balance for Method 3b in kg/s and *t/hr*

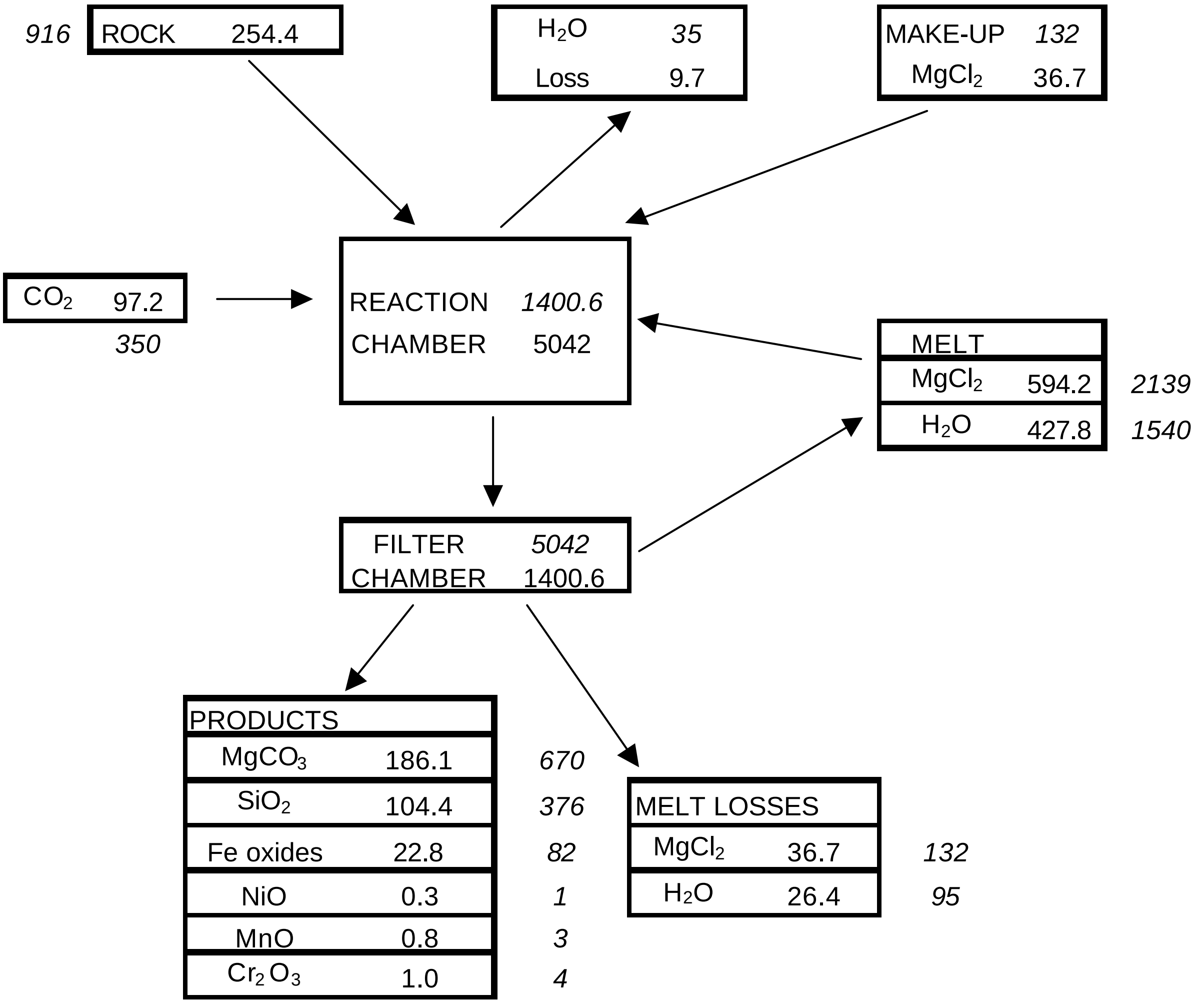


Figure 8.4: Simplified Schematic Showing (A) Method 3b Process and (B) Magnesium Chloride Make-Up Production Process.

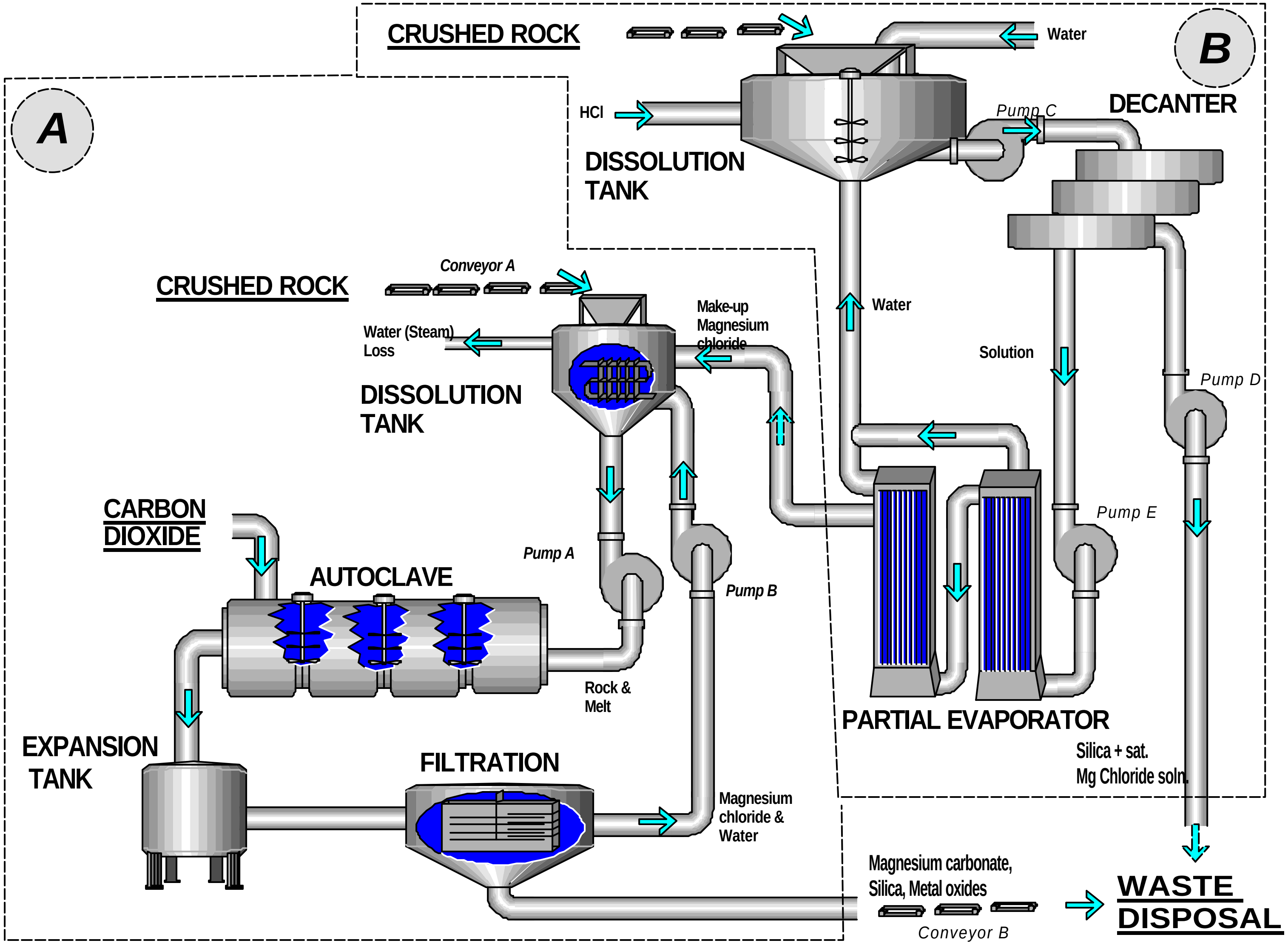
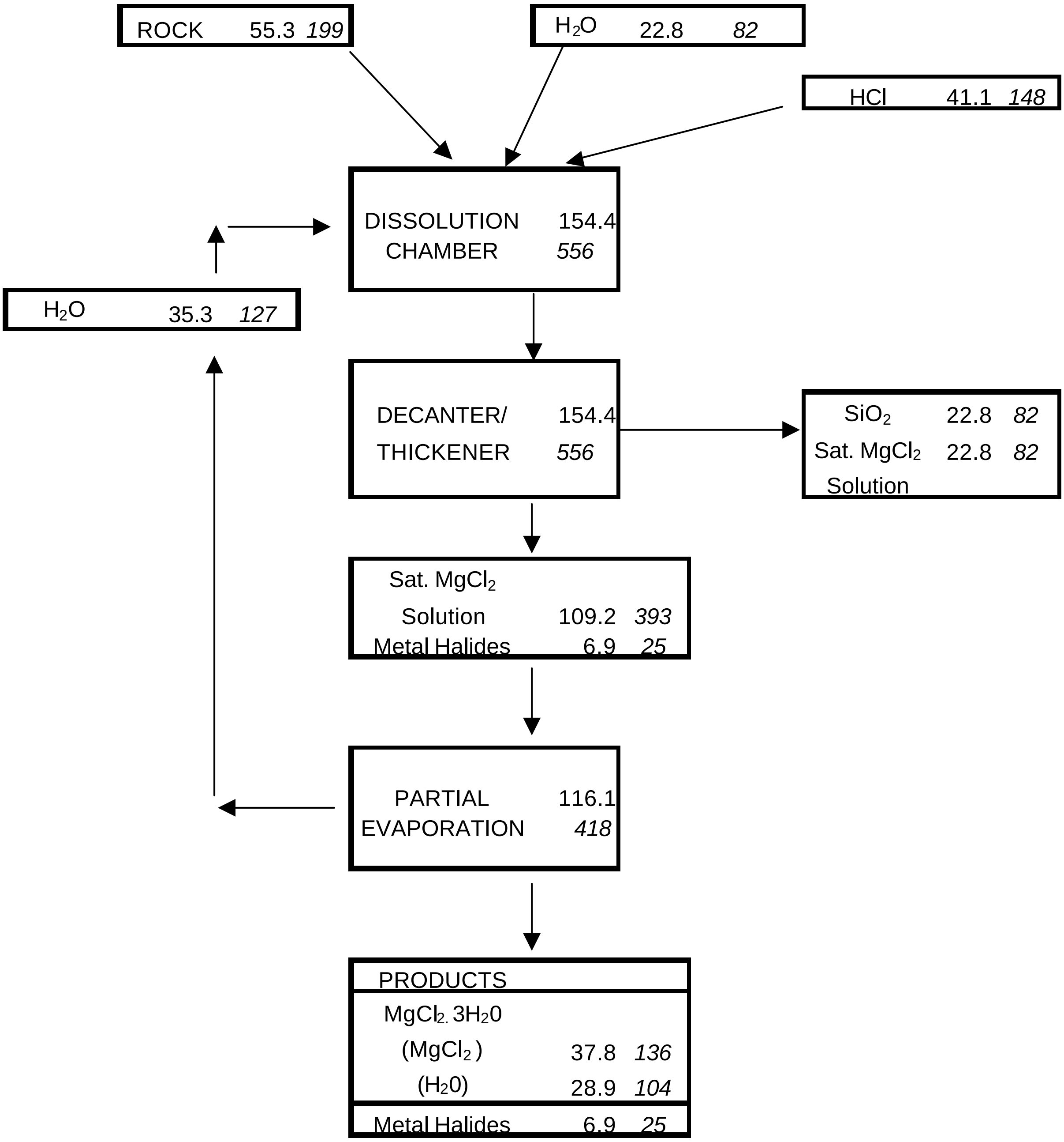


Figure 8.5: Mass Balance $MgCl_2$ Production Facility kg/s (*t/hr*)



Current best bulk price for 36% HCl is £55 (US $88) per tonne ex-works, (ICI Imperial Chemicals UK, August 1999). At this price there would be a cost of £41,435,000 (US $66,296,000) per year for acid. A crushed rock price of US $3/t gives additional costs of £1,905,000 (US $3,050,000).

Additional costs associated with capital, operational and waste disposal lead to comparable overall costs for on-site $MgCl_2$ production to the ex-works price for commercial $MgCl_2$. However, the difficulties of meeting the demand from current world production and the financial and infrastructure costs of transporting commercial $MgCl_2$ may make on-site production the preferred option should a Method 3b plant be instigated.

8.4 Energy Balance

The power hungry process steps of large scale dehydration and drying are absent from Method 3b where the general energy and CO_2 balance appears, within the constraints of unknown kinetics, to be much more favourable than for Method 1.

Energy requirements and generation throughout the Method 3b process, based upon the processing of 916 t/hr of serpentinite rock and 350 t/hr CO_2, are presented in Figure 8.6, whilst Table 8.1 presents the energy balance taking into consideration practicalities of the process.

The theoretical energy balance as shown in Figure 8.6, indicates that the process is essentially energy neutral, with energy inputs balancing with the outputs from the exothermic carbonation reaction.

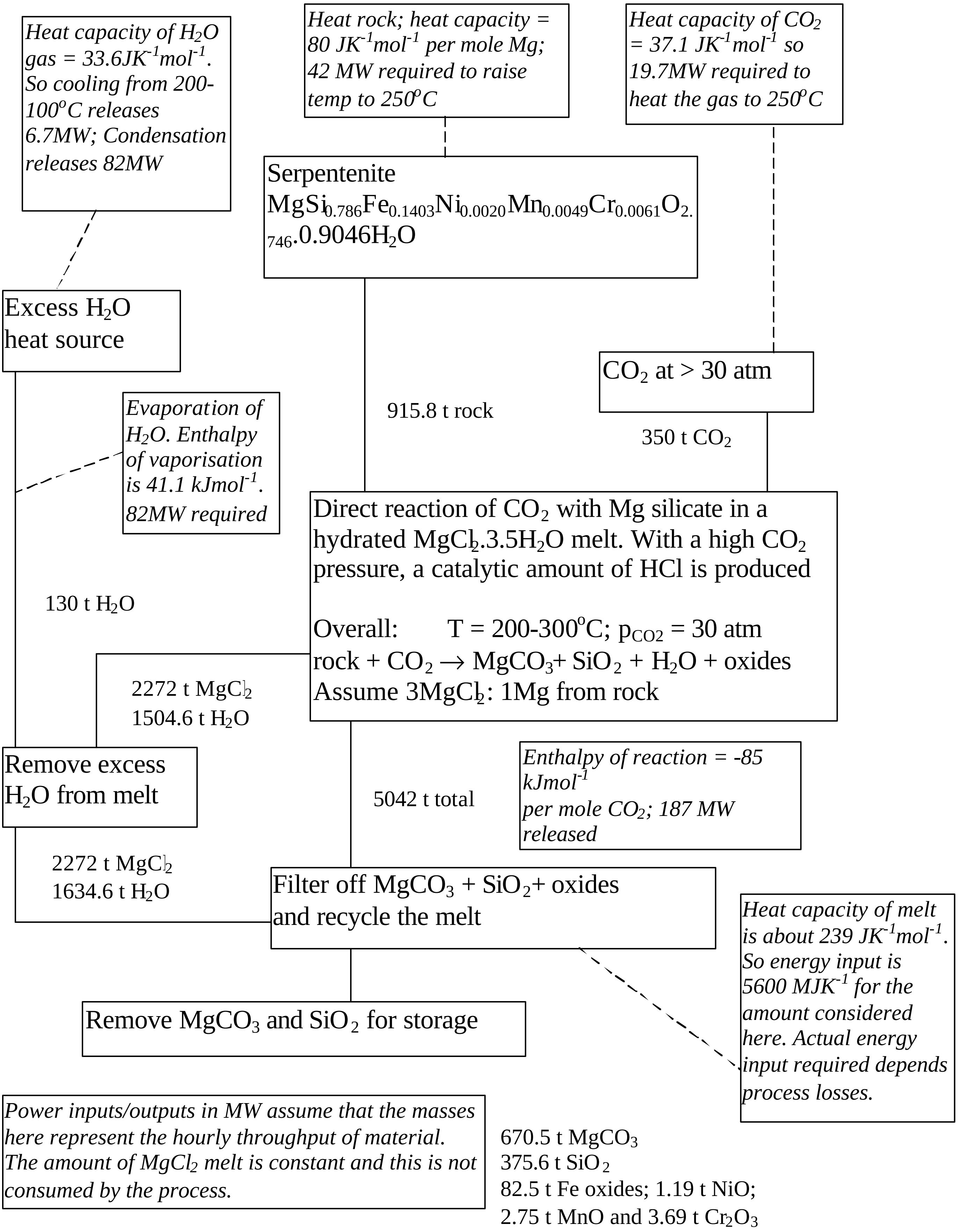
However, the practicalities of the process are such that there will be losses of $MgCl_2$ in the filtration of products from the active melt. The practical energy balance (Table 8.1) indicates the 136 MW energy requirement which would be necessary for the partial dehydration of commercial $MgCl_2.6H_2O$ to the $MgCl_2.3.5H_2O$ form required for the melt.

A further 13 MW would be required to reheat the melt, after losses during processing at 250^oC, to restore the active working temperature. It may be possible to eliminate this 13 MW requirement by running the main carbonation reaction at 300^oC.

Within these constraints Table 8.1 indicates an energy requirement of 149 MW or approximately 30% of the output of the subject power station. This figure makes no allowance for energy usage in off-site production of the make-up $MgCl_2$.

As a final note, the discrepancy between the electrical consumption for mining/quarrying activity between Methods 1 and 3b relates to the use of electromechanical equipment for the 13 Mtpy facility rather than diesel powered plant for the smaller mining operation proposed for Method 3b.

Figure 8.6: Process Energy Requirements and Generation for Method 3b (916 t/hr)



Heat capacity of H_2O gas = 33.6$JK^{-1}mol^{-1}$. So cooling from 200-100°C releases 6.7MW; Condensation releases 82MW

Heat rock; heat capacity = 80 $JK^{-1}mol^{-1}$ per mole Mg; 42 MW required to raise temp to 250°C

Heat capacity of CO_2 = 37.1 $JK^{-1}mol^{-1}$ so 19.7MW required to heat the gas to 250°C

Serpentenite $MgSi_{0.786}Fe_{0.1403}Ni_{0.0020}Mn_{0.0049}Cr_{0.0061}O_{2.746}.0.9046H_2O$

Excess H_2O heat source

CO_2 at > 30 atm

Evaporation of H_2O. Enthalpy of vaporisation is 41.1 $kJmol^{-1}$. 82MW required

Direct reaction of CO_2 with Mg silicate in a hydrated $MgCl_2.3.5H_2O$ melt. With a high CO_2 pressure, a catalytic amount of HCl is produced

Overall: T = 200-300°C; p_{CO2} = 30 atm
rock + $CO_2 \rightarrow MgCO_3 + SiO_2 + H_2O$ + oxides
Assume $3MgCl_2$: 1Mg from rock

Remove excess H_2O from melt

Enthalpy of reaction = -85 $kJmol^{-1}$ per mole CO_2; 187 MW released

Filter off $MgCO_3 + SiO_2$+ oxides and recycle the melt

Heat capacity of melt is about 239 $JK^{-1}mol^{-1}$. So energy input is 5600 MJK^{-1} for the amount considered here. Actual energy input required depends process losses.

Remove $MgCO_3$ and SiO_2 for storage

Power inputs/outputs in MW assume that the masses here represent the hourly throughput of material. The amount of $MgCl_2$ melt is constant and this is not consumed by the process.

Table 8.1: Energy Balance Method 3b (MW)

INPUTS	
ROCK MELT	MAKE-UP H_2O
CO_2	MAKE-UP $MgCl_2$

	GAINS	LOSSES	
Reaction Chamber	Enthalpy of reaction 187	Heat rock	-51
		Heat make-up H_2O and $MgCl_2$	-86
		Heat CO_2	-24
		Losses	-26
SUB TOTAL	187		-187

	GAINS	LOSSES	
Expansion Tank	0	Reheat the melt by 50° C	-13
Filtration	0		
SUB TOTAL	0		-13

	GAINS	LOSSES	
Make-up $MgCl_2$		Partial dehydration of hexahydrate salt	-136
SUB TOTAL	0		-136

TOTAL	187		-336

NET TOTAL	**-149**

A. Energy use in quarrying and comminution of rock and waste disposal/restoration is minimal in comparison with the energy requirement for processing.
This is illustrated in the Carbon Dioxide Balance (Summary) Table 8.3.

B. Losses associated with reheating the melt may be avoided by running the reactor at 300°C rather than 250°C.

8.5 CO_2 Balance

A detailed CO_2 balance for Method 3b is shown in Table 8.2, whilst a summary balance appears in Table 8.3.

From the tabulated data, it appears that the CO_2 balance for Method 3b, within the constraints of unknown kinetics, is generally much more favourable than indicated for Method 1, as the power hungry steps of dehydration and crystallisation as seen in Method 1, are absent. In Method 3b, the carbon dioxide generation is 27.5% of the target of 3 Mt CO_2 sequestered per year. The major contribution is based upon an assumed necessity to partially dehydrate commercial magnesium chloride salts to the $MgCl_2.3.5H_2O$ required for the melt used in this process.

The discrepancy between the masses of CO_2 related to electrical consumption for mining/quarrying activity between Methods 1 and 3b relates to the use of electromechanical equipment for the 13 Mtpy facility rather than diesel powered plant.

8.6 Financial Appraisal

8.6.1 Introduction

The financial criteria used within the evaluation are identical to those considered for the detailed evaluation of Method 1. However, Method 3b is considerably simplified compared with Method 1 and this is reflected in both the capital and operating costs. However, it must be remembered that the kinetics for this process are unknown, although for costing purposes, it has been assumed that the kinetics are comparable with those for Method 1.

In essence, Method 3b requires the processing of 916 t/hr of serpentinite rock for the sequestration of 350 t/hr of CO_2, which is some 40% less than Method 1. This difference is clearly reflected in the costs.

In addition, a financial evaluation has also been considered to include $MgCl_2$ make-up from a separate dissolution plant as discussed in Section 8.3.

8.6.2 Parameters

The spreadsheet and financial summary (Table 8.4) show a total Capital Cost for Method 3b of US $409M. Of this 61% is accounted for by filtration equipment needed to separate the products following carbonation. Appropriate filters are currently available as bolt-together units, although there may be savings to be made through bulk purchase or custom design of large scale units. A more detailed breakdown of the process plant costs is shown in Table 8.5.

Capital costs involved in the rock production i.e. mining/quarrying and comminution are approximately 25% less than those for Method 1 at US $91M compared with US $113.5M.

Table 8.2: Carbon Dioxide Balance for Method 3b for 9 Mtpa

Processing							
	Units	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Dissolution reactors	4	152.5	610	5343600	5343.6	4435	A
Autoclave reactors	16	40	640	5606400	5606.4	4653	A
Filtration	95	60	5700	49932000	49932	41444	A
Conveyors	3	240	720	6307200	6307	5235	A
Pumps	5	317	1585	13884600	13885	11524	A
General plant and office use	1	250	250	2190000	2190	1818	A
		Power MW			**Annual MWh**	**CO_2 t Annual**	
$MgCl_2$ Partial Evaporation		100			876000	613200	B
Plant (As steel/t)	**Initial**	**Over process life**	**CO2/t equiv**	**CO2/t equiv annual**	**Factor re: design, manuf. etc**	**CO_2 t Annual**	
	5000	5000	11500	460	10	4600	C
Quarrying, Crushing, Grinding etc							
	Quantity	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Quarry, electrical usage	1	67	67	586920	587	487	A
					Carbon t		
Diesel Fuel tpa	4453				4000	14,680	
ANFO (explosive) tpa	2000				99	362	
	Rock t/hr	**kW**		**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Comminution	916	14153		123980280	123,980	102,904	A
	Initial	**Quarry life**	**CO_2 t equiv**	**CO_2 t equiv annual**	**Factor re: design, manuf. etc**	**CO_2 t Annual**	
Plant (As steel/t)	1000	2500	5750	230	10	2300	D
Waste Disposal/Resoration							
	Quantity	**Power kW**	**Total**	**Annual kW/h**	**Annual MWh**	**CO_2 t Annual**	
Electrical usage, pumps etc.		67	67	586920	587	487	A, E
					Carbon t		
Diesel Fuel tpa	4453				4000	14,680	E
Plant (As steel/t)	**Initial**	**Project life**	**CO_2 t equiv**	**CO_2 t equiv annual**	**Factor re: design, manuf. etc**	**CO_2 t Annual**	
	1000	2500	5750	230	10	2300	D, E
TOTAL CO_2 Production (t/yr)						**825,109**	

A. At 0.83 t CO_2 per MWh sent out (P Freund, IEA, pers comm 1999). No correction for transmission inefficiency.

B. Evaporation of water and drying of product is achieved by oil heating. Figures are based upon Orimulsion carbon dioxide production of 0.7 tCO_2 /MWh sent out.

C. New carbon steel production is equivalent to 2.3 t CO_2 per t steel. (P Freund, IEA pers. comm. 1999). Factor x 10 for manufacturing, distribution etc.

D. New carbon steel production is equivalent to 2.3 t CO_2 per t steel. Plant replacement = 2.5 x over 25 years and therfore 2500 x 2.3 = 5750t CO2 over 25 years. Factor x 10 for manufacturing, distribution etc.

E. Waste disposal activities are taken as comparable with quarrying, less comminution and blasting.

Table 8.3: Summary Carbon Dioxide Balance, Method 3b

ROCK PRODUCTION	**Source**	**CO_2 t Annual**
Quarrying	Electricity	487
	Diesel	14,680
	Explosives	362
Comminution	Electricity	102,904
Plant	Tonnes steel	2,300
	SUB TOTAL	120,733
PROCESSING		**CO2 t Annual**
Dissolution reactors	Electricity	4,435
Autoclave reactors	Electricity	4,653
Filtration	Electricity	41,444
Conveyors	Electricity	5,235
Pumps	Electricity	11524
General plant and office use	Electricity	1,818
$MgCl_2$ Evaporation	Diesel	613,200
Plant	Tonnes steel	4,600
	SUB TOTAL	686,909
WASTE DISPOSAL/RESTORATION		**CO2 t Annual**
Haulage	Diesel	14,680
Pumping etc	Electricity	487
Plant	Tonnes steel	2,300
	SUB TOTAL	17,467
	TOTAL	**825,109**

Table 8.4: Financial Spreadsheet for Method 3b (excluding $MgCl_2$ make-up facility)

Economic Parameters		
Interest rate	10.0%	
Equity/Loan split	0.0%	
Plant lifetime	25	years
Loan period	20	years
Inflation rate	0.0%	
Rates	1.0%	Installed plant
Insurance	1.0%	Installed plant

Capital Parameters		
Predevelopment	2%	Installed plant
Land cost	5%	Installed plant
Control systems	10%	Installed plant
Contingences	10%	Installed plant
Discount rate	5%	10%
Sequestration price ($/t)	78.65	80.11

Process Stage	Description	Number of Units	Unit Costs ($M)	Installed Plant Cost ($M)	Predevelop Costs ($M)	Land Cost ($M)	Control Systems ($M)	Contingency Costs ($M)	Capital Cost ($M)
1	Mining operations	1	27.521	18.30	0.37	0.92	1.83	1.83	**23.24**
2	Communition - crushing	1	17.140	17.14	0.34	0.86	1.71	1.71	**21.77**
3	Communition - grinding	1	28.790	28.79	0.58	1.44	2.88	2.88	**36.56**
4	Storage/feed hopper	1	1.757	1.76	0.04	0.09	0.18	0.18	**2.23**
5	Dehydrate makeup MgCl	1	0.821	0.82	0.02	0.04	0.08	0.08	**1.04**
6	Dissolution tank	4	1.683	6.73	0.13	0.34	0.67	0.67	**8.55**
7	Autoclave reactor	16	2.693	43.09	0.86	2.15	4.31	4.31	**54.73**
8	Expansion tank	4	1.683	6.73	0.13	0.34	0.67	0.67	**8.55**
9	Filtration	95	2.080	197.60	3.95	9.88	19.76	19.76	**250.95**
10	Conveyors	3	0.084	0.25	0.01	0.01	0.03	0.03	**0.32**
11	Pumps	5	0.166	0.83	0.02	0.04	0.08	0.08	**1.05**
Total				**322.05**	**6.44**	**16.10**	**32.21**	**32.21**	**409.01**

Table 8.4: contd.

Operations parameters		
Fuel cost	**200.00**	**$/t**
Electricity cost	**5.00**	**c/kWh**
Other chemicals	**1.0%**	**Installed plant**
Maintenance - solids	**4.0%**	**Installed plant**
Maintenance - liquids	**2.0%**	**Installed plant**
CO_2 processed	**350**	**t/h**
Rock processed	**916**	**t/h**

Labour parameters		
Operating labour rate	**20.00**	**$/h**
No of shifts	**4**	
Operating time per shift	**1940**	**h/yr**
Supervision	**20.0%**	**labour**
Overheads & Admin	**60.0%**	**labour**

Summary Data			
Process Stage	**Description**	Capital Cost ($M)	**Annual Costs ($M)**
1	Mining operations	23.2	10.4
2	Comminution – crushing	21.8	6.5
3	Comminution - grinding	36.6	16.1
4	Storage/feed hopper	2.2	0.7
5	Dehydrate make-up MgCl	1.0	134.2
6	Dissolution tank	8.6	1.6
7	Autoclave reactor	54.7	4.8
8	Expansion tank	8.6	0.5
9	Filtration	251.0	19.4
10	Conveyors	0.3	0.1
11	Pumps	1.1	0.8
Total		**409.0**	**195.3**

Fuel Consumption (t/yr)	**Fuel Cost ($M)**	**Power Consumption (kW)**	**Electricity Cost ($M)**	**Other Chemicals ($M)**	**Operating Labour per Shift**	**Operating Labour Cost ($M)**	**Supervision Cost ($M)**	**Overhead Cost ($M)**	**Maintenance Cost - Solids ($M)**	**Maintenance Cost - Liquids ($M)**	**Annual Rates ($M)**	**Annual Costs ($M)**
4453	0.89	67	0.03	4.00	15	2.33	0.47	1.40	0.73	0.37	0.18	**10.39**
0	0.00	1374	0.60	0.48	15	2.33	0.47	1.40	0.69	0.34	0.17	**6.47**
0	0.00	12779	5.60	4.33	15	2.33	0.47	1.40	1.15	0.58	0.29	**16.13**
0	0.00	0	0.00	0.02	2	0.31	0.06	0.19	0.07	0.04	0.02	**0.70**
18122	3.62	0	0.00	130.00	2	0.31	0.06	0.19	0.03	0.02	0.01	**134.24**
0	0.00	610	0.27	0.07	3	0.47	0.09	0.28	0.27	0.13	0.07	**1.64**
0	0.00	640	0.28	0.43	4	0.62	0.12	0.37	1.72	0.86	0.43	**4.85**
0	0.00	0	0.00	0.07	0	0.00	0.00	0.00	0.27	0.13	0.07	**0.54**
0	0.00	5700	2.50	1.98	4	0.62	0.12	0.37	7.90	3.95	1.98	**19.42**
0	0.00	225	0.10	0.00	0	0.00	0.00	0.00	0.01	0.01	0.00	**0.12**
0	0.00	1585	0.69	0.01	0	0.00	0.00	0.00	0.03	0.02	0.01	**0.76**
22575	**4.51**	**22980**	**10.06**	**141.38**	**60**	**9.31**	**1.86**	**5.59**	**12.88**	**6.44**	**3.22**	**195.26**

Table 8.5: Method 3b Process Costs

Item	Units	Cost £	Total cost £	Total adjusted cost £	Total adjusted cost US $	Factorised costs US $	Unit cost US$
Storage/feed hopper	1	334,000	334,000	522,918	836,668	1,757,003	1,757,003
Dissolution Tank	4	320,000	1,280,000	2,003,995	3,206,393	6,733,424	1,683,356
Dehydrate make-up $MgCl_2$	1	156,000	156,000	244,237	390,779	820,636	820,636
Autoclave Reactor	16	512,000	8,192,000	12,825,570	20,520,912	43,093,916	2,693,370
Expansion Tank	4	320,000	1,280,000	2,003,995	3,206,393	6,733,424	1,683,356
Filtration	95	1,000,000	95,000,000	95,000,000.00	152,000,000	319,200,000	3,360,000
Conveyors	3	16,000	48,000	75,150	120,240	252,503	84,168
Pumps	8	31,500	252,000	394,537	631,259	1,325,643	165,705
			106,386,000	112,826,165	179,685,196	**379,916,550**	

Assume £1 = $1.60

Factors re. associated activity

Equipment erection	0.45
Piping	0.45
Instrument installation	0.15
Electrical	0.1
Process buildings	0.1
Utilities	0.45
Storage facilities	0.2
Ancillary buildings	0.2
TOTAL	**2.1**

Installed Plant Cost US $	**379,916,550**
Other Costs US $	129,119,528
Total Process Costs	**509,036,078**

The annual operating costs for Method 3b are substantially less than those for Method 1, running at approximately 30% of those for the more complex process. The bulk of the US $195M annual cost relates to the need to supply additional $MgCl_2$ to the process. The theoretical process foresees 100% efficiency in recycling the $MgCl_2$ melt. In practice it is assumed there will be a 2.5% loss of melt in the filtration stage of the process. This requires substantial $MgCl_2$ make-up at a current market cost of US $134M per annum. It should be noted that this represents a significant fraction of current world production.

The major cause for the reduction in annual costs is the elimination of the energy hungry evaporation stage required for Method 1, with the saving of some US $350M.

In summary, Method 3b indicates a sequestration price per tonne CO_2 of US $ 80.11 at a 10% discount rate and US $ 78.65 at a 5% discount rate. The capital costs are US $409M and the annual operating costs US $195M. Costs for waste handling and management for Method 3b are taken as comparable with the mining costs. This adds a further US $4.32 per tonne of CO_2 sequestered, at a 10% discount rate, and $4.24 at a 5% discount rate. Waste disposal and handling in relation to the 3b process with on site production of make-up $MgCl_2$, as disucssed in Section 8.6.3, adds a further US $0.40 per tonne of CO_2 sequestered.

A very cursory study indicates it would be financially beneficial to generate the $MgCl_2$ make-up on site.

8.6.3 On Site Production of $MgCl_2$

A major drawback to Method 3b is the need to buy-in large quantities of $MgCl_2$ to account for process losses. Initial studies indicate this may be overcome by the production on site of $MgCl_2$ for the acid dissolution of serpentinite in a similar manner to that used in the initial stages of Method 1.

A financial spreadsheet for a Method 3b process plant to include a $MgCl_2$ production facility is shown in Table 8.6, whilst the installed plant costs directly associated with this add-on process are shown in Table 8.7.

With regard to capital costs, installation of the $MgCl_2$ production facility increases these over and above those calculated for Method 3b process by approximately 3%, from US $409M to US $422M.

In terms of operating costs, the additional process requires sizeable inputs of HCl, at an annual cost of US $66.7M, although this eliminates the need for commercially sourced $MgCl_2$ and hence generates an annual saving of approximately US $67M.

Allowance has been made in the spreadsheet calculations for the costs associated with the additional rock production required. However, while previously the assumption could be made of disposal costs equivalent to quarrying costs this may not be the case in this scenario.

Table 8.6: Financial Spreadsheet for Method 3b Inclusive of a Magnesium Chloride Make-up Facility

Economic Parameters		
Interest rate	**10.0%**	
Equity/Loan split	**0.0%**	
Plant lifetime	**25**	**years**
Loan period	**20**	**years**
Inflation rate	**0.0%**	
Rates	**1.0%**	**Installed plant**
Insurance	**1.0%**	**Installed plant**

Capital Parameters		
Predevelopment	**2%**	**Installed plant**
Land cost	**5%**	**Installed plant**
Control systems	**10%**	**Installed plant**
Contingences	**10%**	**Installed plant**

Discount rate	**5%**	**10%**
Sequestration price ($/t)	**60.97**	**62.47**

Process Stage	**Description**	**Number of Units**	**Unit Costs ($M)**	**Installed Plant Cost ($M)**	**Predevelop Costs ($M)**	**Land Cost ($M)**	**Control Systems ($M)**	**Contingency Costs ($M)**	**Capital Cost ($M)**
1	Mining operations	1	31.006	18.30	0.37	0.92	1.83	1.83	**23.24**
2	Communition - crushing	1	19.311	19.31	0.39	0.97	1.93	1.93	**24.52**
3	Communition - grinding	1	32.436	32.44	0.65	1.62	3.24	3.24	**41.19**
4	Storage/feed hopper	1	1.757	1.76	0.04	0.09	0.18	0.18	**2.23**
5	Dissolution reactors	3	0.289	0.87	0.02	0.04	0.09	0.09	**1.10**
6	Decanter/thickener	1	1.157	1.16	0.02	0.06	0.12	0.12	**1.47**
7	Dehydration evapourators	3	0.821	2.46	0.05	0.12	0.25	0.25	**3.13**
8	Dissolution tank	4	1.683	6.73	0.13	0.34	0.67	0.67	**8.55**
9	Autoclave reactor	16	2.693	43.09	0.86	2.15	4.31	4.31	**54.73**
10	Expansion tank	4	1.683	6.73	0.13	0.34	0.67	0.67	**8.55**
11	Filtration	95	2.080	197.60	3.95	9.88	19.76	19.76	**250.95**
12	Conveyors	4	0.084	0.34	0.01	0.02	0.03	0.03	**0.43**
13	Pumps	8	0.166	1.33	0.03	0.07	0.13	0.13	**1.68**
Total				**332.12**	**6.64**	**16.61**	**33.21**	**33.21**	**421.79**

Table 8.6: Contd.

Operations parameters		
Fuel cost	**200.00**	**$/t**
Electricity cost	**5.00**	**c/kWh**
Other chemicals	**1.0%**	**Installed plant**
Maintenance - solids	**4.0%**	**Installed plant**
Maintenance - liquids	**2.0%**	**Installed plant**
CO_2 processed	**350**	**t/h**
Rock processed	**1032**	**t/h**
Labour parameters		
Operating labour rate	**20.00**	**$/h**
No of shifts	**4**	
Operating time/shift	**1940**	**h/yr**
Supervision	**20.0%**	**labour**
Overheads & Admin	**60.0%**	**labour**

Summary Data		**Capital**	**Annual**
Stage	**Description**	**Cost ($M)**	**Cost ($M)**
1	Mining operations	23.2	11.6
2	Communition - crushing	24.5	7.3
3	Communition - grinding	41.2	18.2
4	Storage/feed hopper	2.2	0.7
5	Dissolution reactors	1.1	66.7
6	Decanter/thickener	1.5	0.5
7	Dehydration evapourators	3.1	6.8
8	Dissolution tank	8.6	1.6
9	Autoclave reactor	54.7	4.8
10	Expansion tank	8.6	0.5
11	Filtration	251.0	19.4
12	Conveyors	0.4	0.2
13	Pumps	1.7	1.2
Total		**421.8**	**139.6**

Fuel Consumption (t/yr)	**Fuel Cost ($M)**	**Power Consumption (kW)**	**Electricity Cost ($M)**	**Other Chemicals ($M)**	**Operating Labour per Shift**	**Operating Labour Cost ($M)**	**Supervision Cost ($M)**	**Overhead Cost ($M)**	**Maintenance Cost - Solids ($M)**	**Maintenance Cost - Liquids ($M)**	**Annual Rates ($M)**	**Annual Costs ($M)**
5017	1.00	75	0.03	4.51	17	2.64	0.53	1.58	0.73	0.37	0.18	**11.57**
0	0.00	1548	0.68	0.54	17	2.64	0.53	1.58	0.77	0.39	0.19	**7.32**
0	0.00	14397	6.31	4.88	17	2.64	0.53	1.58	1.30	0.65	0.32	**18.20**
0	0.00	0	0.00	0.02	2	0.31	0.06	0.19	0.07	0.04	0.02	**0.70**
0	0.00	120	0.05	66.30	1	0.16	0.03	0.09	0.03	0.02	0.01	**66.69**
0	0.00	200	0.09	0.01	1	0.16	0.03	0.09	0.05	0.02	0.01	**0.46**
30478	6.10	610	0.27	0.02	1	0.16	0.03	0.09	0.10	0.05	0.02	**6.84**
0	0.00	610	0.27	0.07	3	0.47	0.09	0.28	0.27	0.13	0.07	**1.64**
0	0.00	640	0.28	0.43	4	0.62	0.12	0.37	1.72	0.86	0.43	**4.85**
0	0.00	0	0.00	0.07	0	0.00	0.00	0.00	0.27	0.13	0.07	**0.54**
0	0.00	5700	2.50	1.98	4	0.62	0.12	0.37	7.90	3.95	1.98	**19.42**
0	0.00	300	0.13	0.00	0	0.00	0.00	0.00	0.01	0.01	0.00	**0.16**
0	0.00	2536	1.11	0.01	0	0.00	0.00	0.00	0.05	0.03	0.01	**1.22**
35494	**7.10**	**26736**	**11.71**	**78.83**	**67**	**10.40**	**2.08**	**6.24**	**13.28**	**6.64**	**3.32**	**139.60**

Table 8.7: Magnesium Chloride Production Facility Costs

Item	Units	Cost	Total cost £	Total adjusted cost £	Total adjusted cost US $	Factorised costs US $	Unit cost US$
Dissolution Reactors	3	55000	165,000.00	258,328	413,324	867,980	289327
Decanter/thickener	1	220000	220,000.00	344,437	551,099	1,157,307	1157307
Dehydration evaporators	3	156,000	468,000.00	732,711	1,172,337	2,461,908	820636
Conveyors	1	16,000	16,000.00	25,050	40,080	84,168	84168
Pumps	3	31,500	94,500.00	147,951	236,722	497,116	165705
					2,413,562	5,068,480	

Assume £1 = $1.60

Factors re. associated activity	
Equipment erection	0.45
Piping	0.45
Instrument installation	0.15
Electrical	0.1
Process buildings	0.1
Utilities	0.45
Storage facilities	0.2
Ancillary buildings	0.2
TOTAL	**2.1**

Installed plant cost US $	5,068,480
Other costs US$	1,491,330
TOTAL PROCESS COSTS	**6,559,810**

Also, whereas for Methods 1 and 3b, waste metals are predicted to be in the form of oxides, those metals produced in the production of make-up $MgCl_2$ will be as chlorides. Metal chlorides are generally less stable than their oxides and this may result in elevated disposal/treatment costs.

In summary, this method indicates a sequestration price per tonne CO_2 of US $62.47 at a 10% discount rate and US $60.97 at a 5% discount rate. The capital costs are US $422M and the annual operating costs US $140M.

8.7 Sensitivity Analysis

The financial analysis for Method 3b, including a facility to supply make-up Magnesium chloride, indicates a cost of approximately US $62 per tonne of CO_2 sequestered. The greater proportion of these costs are generated in relation to the process plant capital costs and costs associated with the supply of make-up chemicals.

Costs, both financial and environmental, associated with fuel and power consumption are of significant interest given the nature of the project.

While the authors by no means consider that the figures presented in the financial spreadsheets represent worst-case scenarios, it is possible that overall costs may be reduced through the use of other existing or developing technologies.

Specifically, personal communication with Lackner (1999) suggest significant savings may be possible through the utilisation of the heat of exothermic reactions as process heating. Also Wendt (1999) in an internal Los Alamos National Laboratory report suggests that the need for make-up $MgCl_2$ may be significantly reduced through the use of multistage continuous counter current decantation processes.

Rather than attempt to quantity detailed costs and benefits associated with the use of such technologies, a simple sensitivity analysis was performed using varied values for process plant capital costs, fuel consumption, power consumption and make-up chemical costs.

8.7.1 Sensitivity Analysis Method

The four parameters described above were considered, i.e.:

- Process plant capital costs
- Fuel consumption
- Power consumption
- Make-up chemical costs.

For each of these, costs per tonne of CO_2 were recalculated on the basis of rates which represented:

- Rises in costs up to 150% of those presented in the financial spreadsheet
- Reduction in costs up to 25% of those presented in the financial spreadsheet.

Costs were recalculated for presumed discount rates of 5 and 10%.

Costs associated with the mining and comminution of the source rock material were not included as confidence in these costings is high.

8.7.2 *Sensitivity Analysis Results*

Results from the sensitivity analysis at 5% and 10% discount rates are shown in Figures 8.7 and 8.8.

The most significant factor in the overall costing relates to capital costs for the process. A reduction by half in capital costs produces a saving of approximately US \$14 per tonne of CO_2 sequestered while a further halving of capital costs produces a final price of US \$42.06. However, this saving may be unrealistic, as should the introduction of additional or more complex plant be necessary, then increases in plant costs will occur. This amounts to an overall cost increase for the process of approximately US \$10 per tonne of CO_2 sequestered for each 25% increase above the capital costs presented in the spreadsheet.

The commercial availability of make-up $MgCl_2$ and the costs associated with its purchase, or on-site manufacture, are a significant proportion of the overall costing. For each 25% reduction in $MgCl_2$ make-up requirement there is a saving of approximately US \$5 per tonne of CO_2 sequestered at a 5% discount rate and approximately US \$5.5 saving at a 10% discount rate. If the requirement for make-up $MgCl_2$ were reduced to 1%, then the cost per tonne of CO_2, assuming no other savings, would be approximately US \$40, or approximately twice the target CO_2 sequestration figure of US \$20 per tonne.

From the results, at 5% discount rate, it is clear that any savings made through utilisation of reaction heat, and hence a reduction in fuel and power consumption, are comparatively negligible. A reduction in consumption of both of these commodities by 75%, i.e., to 25% of original costings, results in a sequestration cost gain totalling US \$2.64 per tonne CO_2 sequestered. At the 10% discount rate the saving is almost identical.

8.7.3 *Sensitivity Analysis Conclusions*

The sensitivity graphs give an indication of the effects on the overall costings through the variation of individual parameters. In practice it is unlikely that only one parameter would vary, either for better or worse. In order to meet the target figure of US \$20 per tonne of CO_2 sequestered would require substantial reductions in all four parameters considered.
By way of illustration, Table 8.8 presents one scenario which would approach the target figure. Here it is assumed that capital costs have been reduced by 67%, power consumption.

Figure 8.7:Process plant sensitivity for Method 3b with $MgCl_2$ make-up facility, 5% discount rate, relative to the spreadsheet costs in Table 8.6

Percent	150	125	100	75	50	25
Capital	81.45	70.53	61.13	53.25	46.89	42.06
Fuel consumption	62.12	61.63	61.13	60.63	60.13	59.64
Power consumption	61.89	61.51	61.13	60.75	60.36	59.98
Make-up chemicals	71.94	66.53	61.13	55.72	50.32	44.91

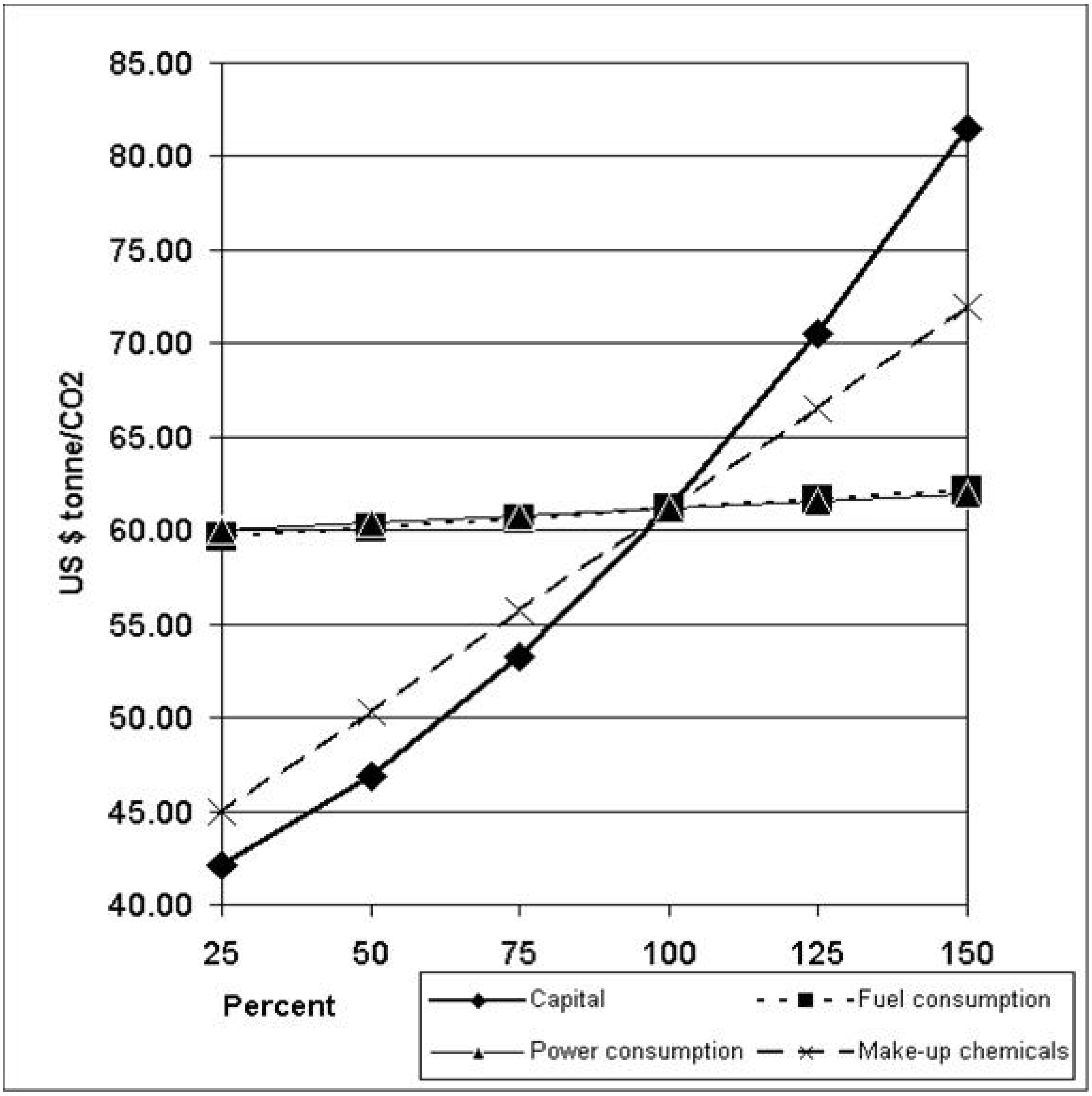
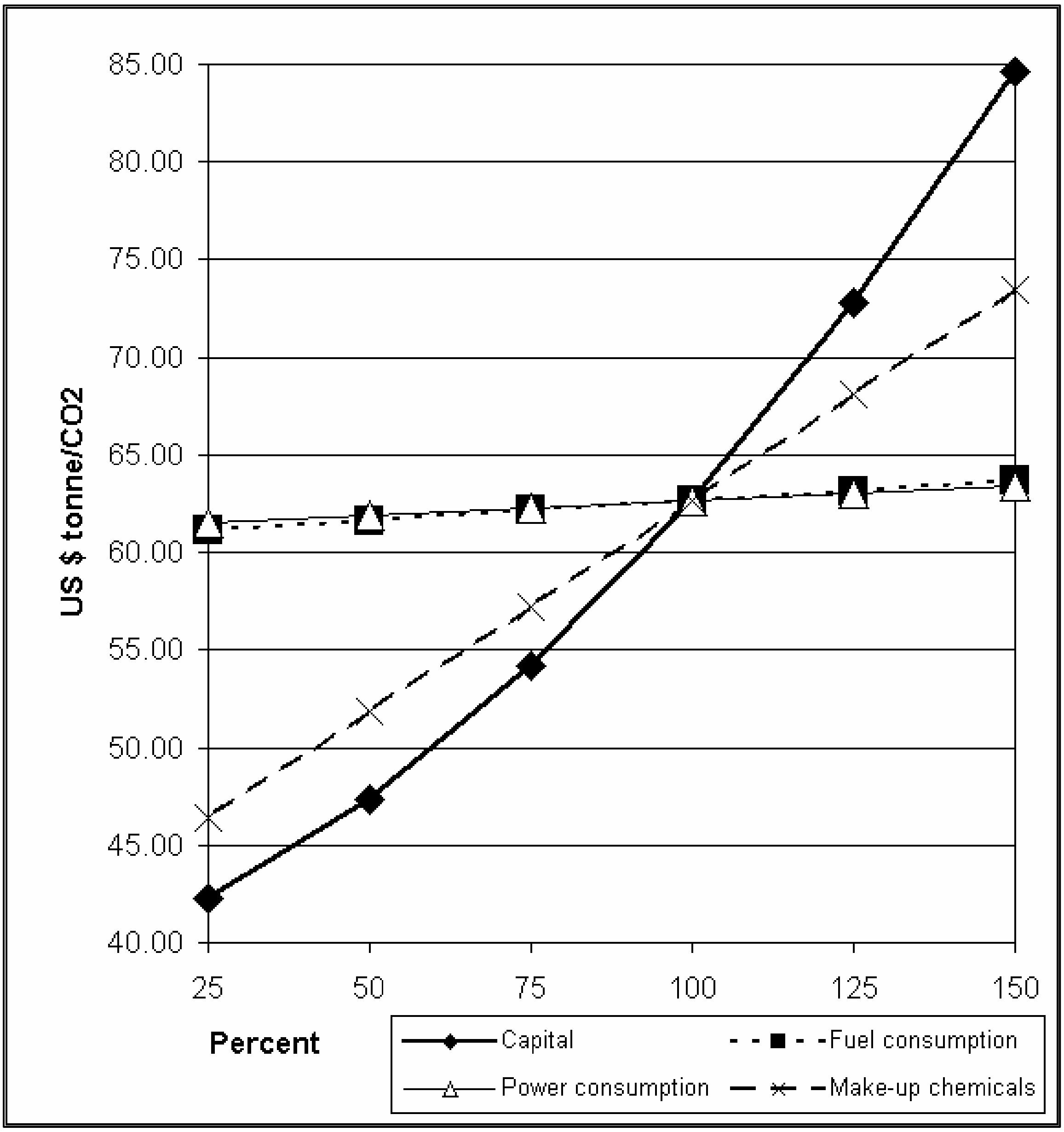


Figure 8.8: Process plant sensitivity for Method 3b with $MgCl_2$ make-up facility, 10% discount rate, relative to the spreadsheet costs in Table 8.6

Percent	**150**	**125**	**100**	**75**	**50**	**25**
Capital	84.61	72.79	62.64	54.16	47.35	42.22
Fuel consumption	63.63	63.14	62.64	62.14	61.65	61.15
Power consumption	63.41	63.02	62.64	62.26	61.87	61.49
Make-up chemicals	73.45	68.05	62.64	57.23	51.83	46.42



by 67% and both fuel consumption and the need for make-up $MgCl_2$ by 95%. Whether sufficient heat from exothermic reactions and retention of $MgCl_2$ within the system could reach this level of efficiency within the constraints of a major mineral processing operation is open to question.

Table 8.8: Reduction in costs, from 100%, in process operations required to achieve a sequestration process cost of US $20/tonne CO_2

Process sensitivity parameters, not including mine operations		
Capital cost Fuel consumption Power consumption Other chemicals	100% 100% 100% 100%	
Discount rate	5%	10%
Sequestration price ($/t)	**61.13**	**62.64**
Process sensitivity parameters, not including mine operations		
Capital cost Fuel consumption Power consumption Other chemicals	33% 5% 33% 5%	
Discount rate	5%	10%
Sequestration price ($/t)	**19.99**	**20.22**
N.B. These figures include no allowance for waste disposal/management		

8.8 Conclusions

The results from this brief study of the kinetically unproven method of CO_2 sequestration have shown that although overall capital and operating costs can be significantly reduced in comparison to Method 1, and that the cost per tonne of sequestered CO_2 can be greatly reduced (down to approximately $60/t in comparison to >$200/t), the viability of such a method remains in doubt.

A particular stumbling block lies with the large volumes of HCl required as part of the make-up $MgCl_2$ facility, which in its own right may render the process untenable. However, if this modified approach is not adopted, a commercial supply of $MgCl_2$ in the make-up volumes required is also thought to be an unrealistic target.

The sensitivity analysis has shown that although it is possible to reach the target cost of around US $20 per tonne of CO_2 sequestered by this method, the economies to the process costs need to be very substantial.

In conclusion, assuming that the kinetics of the reactions are satisfactory, the possibility of developing this method on a commercial basis appears problematic, without substantial improvements in overall efficiency and plant design.

9.0 DISCUSSION

9.1 Introduction

Considerable efforts have been made in recent years to investigate the possibility of storing CO_2 as a stable mineral carbonate. A number of different starting products have been suggested including magnesium and calcium silicates, brines, and carbonates themselves.

Most previous studies have concentrated on the concept of sequestration, often with some thermodynamic and kinetic data, but without attempting to follow any of the processes through to conclusion by undertaking a fully costed feasibility study.

This report has studied six different mineral carbonate sequestration routes, and in addition, has undertaken a more detailed study of two of the most favourable methods.

In summary, the various methods investigated were:

- Method 1 – Reaction with magnesium hydroxide produced from acid dissolution of a suitable magnesium-rich silicate rock;
- Method 2 – Reaction with magnesium hydroxide produced from dehydration of magnesium-rich brine;
- Method 3a – Reaction with magnesium hydroxide produced from dissolution of magnesium silicate rock in magnesium chloride melt;
- Method 3b – Direct carbonation from dissolution of magnesium silicate rock by magnesium chloride melt;
- Method 4 - Reaction with calcium hydroxide produced from dissolution of a suitable calcium-rich silicate rock, and
- Method 5 – Reaction of pressurised CO_2 with seawater-dissolved dolomite.

Before a discussion of the important aspects of the two methods which have been studied in detail (Methods 1 and 3b), it is worth briefly considering the reasons why the four alternative methods were not thought to be viable propositions.

9.2 Rejected Methods

Several methods were considered at a preliminary level (Section 5), but rejected for more detailed investigation for a variety of reasons:

Method 2: This method relies on the extraction of pure, saturated $MgCl_2$ from naturally occurring brine, which is then converted to powdered hydroxide before being reacted with CO_2. $MgCO_3$ and $HCl_{(aq)}$ are the main products, with the former stored at surface, whilst the latter is re-injected underground. This, in effect, is a modification of Method 1, but fails for a number of reasons. These include the fact that naturally occurring brines of suitable chemistry are rare in nature, enormous volumes of brine are required for the process, and if taken from evaporite sequences, are likely to cause severe surface subsidence, the process contains a major, energy intensive, dehydration phase, and the process generates huge volumes of HCl which must be disposed of either at surface or returned underground. Neither option is environmentally acceptable.

Method 3a: In an effort to reduce the major dehydration stage faced by many of the methods, it has been proposed (Wendt *et. al.* 1998b) that a $MgCl_2.nH_2O$ (n = 3.5) melt may be used as a solvent either for the synthesis of $Mg(OH)_2$ or for direct carbonation of silicate rock (Method 3b). Thus, for this method, fine Mg silicate rock is dissolved in molten hydrated $MgCl_2$ (which is recycled), and reacted with CO_2, with disposal of $MgCO_3$, SiO_2 and bi-products. However, investigation of the process was not taken further as it was believed that the process incorporated two serious energy consuming steps, most notably the partial dehydration of the feed (elevate temperature to 600°C) before dissolution, and the evaporation stage. These are in addition to the fact that the reaction kinetics are also unknown.

Method 4: This method utilises Ca silicate rock as the feed, which is dissolved in HCl, and then converted to powdered hydroxide. This is then dissolved in H_2O, and then reacted with the CO_2, with disposal of $CaCO_3$ and SiO_2 products. This method was deemed unsuitable at the preliminary stage due to the extremely large volumes of water which would be required for the hydration of $Ca(OH)_2$ (estimates of approximately 0.5 Mt per hour have been made), and as a result of these fluid volumes, tailings lagoons for the process would be enormous. More importantly, there is an inability to practically filter and recharge the huge volumes of limewater which would be generated in order to meet CO_2 demands.

Method 5: This method is based on the dissolution of $MgCO_3$ from dolomite in seawater, which is reacted with CO_2 at 10 atm to produce $MgCl_2$ and $NaHCO_3$ in solution. The latter is precipitated by adding a large amount of NaCl, before being removed along with the $CaCO_3$. The excess NaCl and $MgCl_2$ are disposed of to the sea, whilst the solids are stored on land. Although the basic chemistry and thermodynamics of the process are proven, the volumes of solution, magnitude and cost of the plant to deal with them, and the potential environmental impact of oceanic discharge, render this method unfavourable.

9.3 Chosen Methods

Two methods (Methods 1 and 3b) were selected for a detailed financial appraisal, although only Method 1 was evaluated to the level of sensitivity as required by the contract, as the unknown kinetics for Method 3b necessitated the assumption of several key parameters.

The detailed study of Method 1 produced disappointing results with regard to the sequestering potential of the method, as both the cost and overall efficiency of the process are unacceptable. The key points are:

- An enormous energy requirement is needed for the dehydration and crystallisation stages which in practical terms equates to a requirement of more than four times the amount of

energy produced by the 500 MW power station for which the process has been designed to accommodate, and
- Make-up HCl is required to constantly replenish the reactants for the dissolution stage. For the proposed method, this extra acid represents nearly a third of annual world production.

These two factors taken together contribute to an overall sequestration cost of in excess of US $200 per tonne of CO_2, but more importantly, the process emits more CO_2 than it sequesters.

From the design parameters, it is not readily obvious where significant savings could be met without a radical alteration to the flowsheet, and in particular, the energy hungry dehydration step. Even with novel technology, it is unlikely that this fundamental hurdle can be overcome.

In contrast, Method 3b attempts to avoid the energy intensive steps detailed above by a direct carbonation process. Although the method is kinetically unproven, by assuming kinetics similar to those adopted for Method 1, it is possible to evaluate the process.

The basic capital and operating costs of the process are significantly less than those ascribed to Method 1, whilst the overall sequestration cost is also much reduced. However, this economy comes with a serious problem of substantial $MgCl_2$ make-up to replenish the losses incurred by the process. If this material is bought in, the amounts required are well in excess of annual world production, whilst if a $MgCl_2$ make-up plant is incorporated, huge volumes of HCl are required to supply this.

Either way, considerable logistical problems arise, and again, without major modification and improvements to the process, it seems unlikely that the method could be made commercially viable.

In conclusion, this study has shown that without radical alteration to the various process routes, it seems unlikely that CO_2 sequestration within a stable mineral carbonate is a realistic proposition. For either of the main two processes to have a chance at success, the energy hungry dehydration stage in Method 1, and the reliance on huge volumes of make-up chemicals in Method 3b, must be overcome. Further research should thus be targeted at these specific problems.

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