Ca AND Mg EXTRACTION FROM INDUSTRIAL MINERALS FOR THE SEQUESTRATION OF CARBON DIOXIDE

(LABORATORY EXPERIMENTS)

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SUMMARY

Introduction

In the framework of the project "Project Plan CATO: CO_2 capture, transport and storage" experimental laboratory research on carbon dioxide sequestration by mineral carbonation has been carried out by Geochem Research. Initially the work was focused on direct carbonation and magnesium extraction by nitric acid. In agreement with TNO Science and Industry it was decided to leave out the direct carbonation and to perform research on the use of other mild extracting agents: acetic acid, sodium pyrosulphate and sodium sulfate. The work done on nitric acid was divided in magnesium extraction experiments and nitric acid recycling experiments.

The mineral used for magnesium extraction was olivine, Ca-rich plagioclase was used in some experiments in order to test its suitability for mineral sequestration of carbon dioxide.

Various ways of carbon dioxide sequestration were tried using the products from the above mentioned experiments.

Acetic Acid, Potassium Pyrosulphate and Sodium sulphate.

Mild extraction was performed in an 600 ml Parr autoclave at temperatures ranging from 150°C to 250°C. Purpose of the experiments was to test the extracting properties of the chemicals as well as to produce a magnesium solution that could be used directly for carbonation.

Of all the chemicals, only potassium pyrosulphate produced a solution that contained a considerable amount of magnesium. Non of the products obtained was suitable for direct application.

Nitric Acid.

Nitric acid extraction of magnesium from olivine was performed in a one litre double walled glass vessel at temperatures ranging from 60-90°C. The extreme solubility of magnesium nitrate enables the production of concentrated and supersaturated magnesium nitrate solutions (up to 84 g/l and probably higher). Solutions of lower concentration offer the possibility for Fe-removal by crystal fractionation. Filtration of the silica proceeds quicker at higher concentrations and longer reaction duration.

The reaction rate of (commercially available) Ca-rich plagioclase is considerably lower than that of olivine. Combined with the fact that its sequestrating capacity is low, this mineral offers little perspective on future use for mineral carbonation.

Magnesium nitrate decomposition.

Magnesium nitrate hexahydrate was decomposed in a 600 ml Parr autoclave connected to a 2 litre autoclave, which served as a condensation vessel.

Magnesium nitrate hexahydrate decomposes at a temperature of 350°C. The decomposition is non linear, which means that it takes long to remove the last nitrate groups at this temperature. Nitric acid was recycled with concentrations up to 10 M. The decomposition products obtained were a mixture of magnesium oxide, a basic magnesium nitrate and magnesium hydroxide. Nitrate removal percentages were as high as 90 %.

Carbon dioxide sequestration.
Three ways of carbon dioxide sequestration were attempted: simultaneous distillation and carbonation of an acidic magnesium nitrate solution, simultaneous thermal decomposition and carbonation of magnesium nitrate hexahydrate and aqueous carbonation of the Mg-rich decomposition product. Simultaneous distillation and carbonation did not work. Simultaneous decomposition and carbonation gave promising results. During aqueous carbonation hydromagnesite was formed. It was also observed that in a alkaline environment at low to moderate temperature carbon dioxide can replace nitrate groups to an certain extent.

Conclusion.
Together with the HCl extraction route, magnesium extraction by nitric acid seems to be one of the more effective means to produce a material suitable for carbon dioxide sequestration. Nevertheless, a considerable amount of energy is needed for the decomposition of the nitrates. In the present research it has been observed that carbon dioxide can, under certain circumstances, replace nitrate in a basic magnesium nitrate solution. It could be useful to further investigate and optimize this process in order to obtain an economically sound way to perform mineral sequestration on carbon dioxide.

Due to the high cost of mining, transportation and processing, the surface mineralization of carbon dioxide will probably not be economically feasible. Certainly not at a very large scale. However, the research on this matter can be used for the development of carbon dioxide friendly methods for the production of magnesium products. With olivine replacing magnesite as a raw material for the production of refractories already 5 Mtpy of carbon can be saved, not to mention the reduction of the production energy needed.

1 GENERAL INTRODUCTION

A lot of research has been carried out on the mineral sequestration of carbon dioxide. Most, if not all methods for mineral sequestration investigated are not likely to be economically feasible. In the present research programme some new sequestration routes were tried and some old routes were re-investigated.

There are two widely investigated methods of sequestration, a two step model during which magnesium is first extracted from the mineral, subsequently separated and finally carbonated, and a single step, direct sequestration of olivine at high pressure and temperature. For the two step reaction strong acids are used which are recycled. The whole process involves some very aggressive stages during which extremely hot acidic fumes are produced. Direct carbonation on the other hand is less aggressive but proceeds very slowly.
Initially Geochem's work was focused on two step sequestration using nitric acid and direct carbonation experiments at high temperature and high pressure. However, in agreement with TNO Science and Industry is was decided to leave out the direct carbonation route. The research already performed by others was very extensive and it seemed pointless to try and improve this. Instead, it was suggested to try other new or hardly researched mild extraction routes to see if they could be promising.

To avoid both the very aggressive laborious acid reclamation and the slow reaction rates, new ways were proposed using different extraction media. It was argued that whenever acid would be used that would react faster than carbon dioxide and at the same time less aggressive than hydrochloric acid, disadvantages of both methods could be levelled out. In addition, it was considered to investigate the extraction and recycling properties of nitric acid in the magnesium extraction and carbonation experiments.

In the present programme the following magnesium extraction routes were investigated:

- Mild extraction of magnesium using acetic acid and olivine
- Mild extraction of magnesium using potassium pyrosulfate and olivine
- Mild extraction of magnesium using sodium sulfate and olivine
- Extraction of magnesium using nitric acid and olivine
- Extraction of calcium using nitric acid and Ca-rich plagioclase

The magnesium extracts from the nitric acid experiments were used for various nitric acid recycling and carbon dioxide sequestration tests.

The minerals used in published research are mostly: olivine, calcium rich plagioclase and serpentine. These were chosen for the following reasons:

- They exhibit high weathering rates
- They are widely available
- They contain the right anions for carbonation

Compared to each other, these minerals do have their specific advantages and disadvantages. Their eventual application will therefore depend on location with respect to the quarry and sequestration method chosen. For this research only olivine and plagioclase were used, mainly because they do not need thermal pre treatment and because they are amply available in Europe.

2 MAGNESIUM EXTRACTION FROM SILICATES BY ACETIC ACID, POTASSIUM PYROSULFATE AND SODIUM SULFATE

2.1 Introduction.

Dissolution of olivine in weak acids or weak bases proceeds very slowly and it can take several days before sufficient magnesium for carbon sequestration has gone into solution. In order to speed up the reaction rate it was decided to carry out all mild extraction experiments in an autoclave at temperatures ranging from 150 to 250°C.

2.2 Methods used.

All autoclave experiments were conducted in a 600 ml Parr 4560 autoclave (carpenter alloy 20Cb-3) mixed by a magnetic coupled single propeller stirring rod. The autoclave was heated in a 780 watt heating mantle and controlled by a Parr 4842 console.

Fig 2.1: Autoclave set up as used for the magnesium extraction

Two modes of heating are possible, at two 'low' capacity resulting in ±3°C/min and 'high' capacity resulting in ±6°C/min. Reagents were weighed and mixed in a glass liner, the liner was placed in the autoclave. Depending on the experiments the autoclave was not flushed, flushed with nitrogen or flushed and filled with carbon dioxide. All experiments were performed at maximum stirring speed of 600 rpm. At the end of the experiment the reactor was tap water cooled to a temperature below 70°C in approximately 20 minutes. The total contents of the autoclave including the liner were weighed and the pH was measured. The effluent and silica were separated by decantation and subsequently filtered in a 7,5 cm diameter büchner funnel using 7 cm diameter Whatman No 5 filters. The silica was dried at a temperature of 110°C. The mineral residue was washed, dried and weighed. The filtrate was analysed for Mg^{2+} by using a Dr Lange LASA 20 Sensor Array Photometer and a Dr Lange cuvette-test LCK 326. Dilutions for these analyse were made using analytical grade water (CAS No 7732-18-5) supplied by Fisher Scientific.

2.3 Acetic acid extraction of Mg^{2+} from olivine

Acetic acid is a relatively mild organic single proton acid (CH_3-COOH), with a molecular weight of 60,05. The acetic acid used for experiments was 96% pro analysis quality by Merck. Acetic acid is very volatile and easily forms explosive mixtures with air from 40°C, it's auto ignition point lies at 427°C. Reaction between olivine and acetic acid is as follows:

eq. 2.1: $4CH_3\text{-}COOH\ (aq) + (Mg,Fe)_2SiO_4\ (s) \rightarrow 2Mg^{2+}\ (aq) + 4CH_3\text{-}COO^-\ (aq) + H_4SiO_4\ (s)$

Magnesium acetate is, according to the Handbook of Chemistry and Physics, a very soluble and hygroscopic salt. This means that the concentration to be used for the experiments is determined by the progression of the reaction. In a highly concentrated acetic acid there will be hardly enough H_2O for the acetic acid to be protonized. Therefore a reaction mixture of 50% demineralised water and 50% acetic acid was chosen.

The olivine used was 100-300µ AFS 50 grit blasting olivine produced by AS Olivin in Norway. Its chemical composition is given in table 2.1.

MgO	49,0 %	Al_2O_3	0,50 %
SiO_2	41,0 %	NiO	0,35 %
Fe_2O_3	7,0 %	MnO	0,10 %
Cr_2O_3	0,4 %	CaO	0,05 %
Percentage inert minerals 5,2 - 7,3 %*			

Table 2.1: Chemical composition of Olivine AFS 50 (data from Kurt Freytag and * from Jonckbloedt 1997).

Reagent	Molecular weight	Mole	Gram
Olivine (Mg_2SiO_4)	140,1	0,46	64
Acetic acid (CH_3-COOH)	60,05	1,67	100
H_2O	18	5,56	100

Table 2.2: Reaction mixture proportions of olivine/acetic acid reaction.

Looking at equation 1 and table 2.2, 100 ml of acetic acid could theoretically dissolve 58 grams of olivine. For the recipe used in the experiments, in table 2.2 an extra 10% of olivine is added to compensate for the non reactive minerals.

Considering the organic nature of acetic acid and its possible decomposition at higher temperatures, it was decided to perform the experiments at 150°C to begin with. At first, experiments were performed under slow heating conditions in order to keep a close look on a possible sudden increase of temperature. Given the weak acidity, a reaction time of 3 hours was chosen. Experimental parameters are given in table 2.3.

exp no.	olivine	ac. acid	water		C°	duration	remarks
	gr	gr	gr	pH		(hours)	
1	64	106	99	2	150	3	air
2	0	106	100	2	150	3	no olivine
3	64	104	99	2	150	3	nitrogen
4	64	105	99	2	175	3	nitrogen
5	64	105	99	2	150*	3	nitrogen, turkish micro olivine

Table 2.3: Parameters of the acetic acid experiments performed,
***= temperature peaked to 175°C for ± 5 minutes.**

2.3.1 Results and observations.

The experimental results are given in table 2.4. A first experiment was conducted according to the general experimental information. After three hours at 150°C and cooling period, the autoclave was opened. Much of the liner and the reaction mixture was coloured bright orange red. It was assumed that this colour was caused by oxidation of the Fe^{2+} content originating from the dissolved olivine. In order to be sure that this colouring was not caused by dissolution of the autoclave interior, an experiment (number two) was conducted without olivine. This experiment showed that the colouring was indeed caused by the iron from the olivine. To prevent further colouring of the reaction products, the autoclave was four times flushed with 10 bar nitrogen for the remaining experiments.

The third experiment is a copy of the first experiment except that the autoclave is being flushed with nitrogen. The silica formed was separated in two steps, the first portion of silica was decanted with the effluent, filtered and dried. The second (small) portion was separated by decanting and filtering the wash water used for the residue.

Compared to the first experiment the results of the third experiment were disappointing, therefore, for the fourth experiment, the reaction temperature was increased to 175°C. This time the silica was separated in one single batch.

The fifth and last experiment was performed to see if a finer grain size would significantly enhance the reaction. Turkish filter dust olivine was used with a grain size < 65µ. The Turkish olivine reacted vigorously and although the experiment temperature was set at 150°C the exothermic reaction caused the temperature to peak briefly at 175°C. After opening the reactor it was visible that the olivine and silica had formed an inseparable mixture. Consequently the olivine consumption could not be estimated. Nevertheless, the Mg^{2+} concentration in the filtrate was the highest achieved in all the acetic acid experiments performed.

exp no		filtrate	residue	silica	Silica colour	olivine consumed	Mg in opl
	pH	gr	gr	gr			gr/l
1	3,5	178,8	52,31	6,06	bright orange	18 %	17,50
2	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.
3	3,4	206,9	55,61	4,42	grey/pink[1]	13 %	11,50
4	3,6	212,3	51,13	5,15	faint pink	20 %	15,00
5	3,7	206,6	40,8	15,39	grey,pink,orange[2]	n.a.	26,00

Table 2.4: Data of the reaction products formed from the olivine-acetic acid reaction,
1) colours of the first and second silica separated,
2) no satisfactory separation possible.

The filtrate was coloured slightly yellow at lower temperature (150°C) and yellow/orange for both experiments respectively at higher temperature (175°C) and with the Turkish olivine fines. For each experiment the filtrate was stored in two separate bottles of 100 ml of which one was not completely filled. After a few hours both bottles would change colour to orange/brown, the one containing more air becoming darker than the one that was completely filled up. In bottles that were exposed to the open air, a dark flaky precipitate would form.

2.3.2 Discussion.

At first glance the results indicate that acetic acid is suitable, although modestly, for olivine dissolution. It is clear that the reaction, regardless the extent of neutralization, is buffered around pH 3,4 - 3,7. Higher reaction rates can be obtained by either using smaller grain sizes or by increasing the reaction temperature. Both are not favourable for the process: where smaller grain sizes will greatly increase the cost of milling, a higher temperature destabilizes the acetic acid. In both experiment 4 and 5, the first kept at 175°C for three hours and the second peaking at 175°C, black flakes are formed. Although unfavourable for the quality of the precipitating silica, the reaction proceeds quicker under oxidizing atmosphere. This is also reported by Velbel 1999, who writes that minerals containing elements vulnerable to oxidation, have higher weathering rates in oxidizing environments than other minerals from the same solid solution sequence.

2.4 Potassium pyrosulphate extraction of Mg^{2+} from olivine

Potassium pyrosulphate ($K_2S_2O_7$) in solution forms potassium disulphate ($KHSO_4$) which acts as a relatively strong single proton acid with a p-value of 1,92. It has a molecular weight of 254,31 and a solubility of 363 g/l in cold water and 1216 g/l in hot water (handbook of chemistry and physics). It reacts with olivine in the following way:

eq. 2.2: $4KHSO_4\,(aq) + Mg_2SiO_4\,(s) \rightarrow 2Mg^{2+}\,(aq) + 4K^+\,(aq) + 4SO_4^{2-}(aq) + H_4SiO_4\,(s)$

For optimum magnesium extraction the first experiment was performed using an $K_2S_2O_7$-solution saturated at 20°C. At first, the proportions of the reactants were kept comparable to the previous acetic acid experiments, although this implied quite an over measure of olivine. After three hours of reaction time the autoclave was tap water cooled and opened.

exp no	olivine (gr)	$K_2S_2O_7$ solution (gr)	pH	$K_2S_2O_7$ concentration	T(°C)	Time (hrs)	atmosphere
6	64	246,4	n.a.	sat. at 20°C	150	3	4x N2
7	64,07	215,29	0,598	128g/l	150	3	4x N2
8	9,99	216,55	0,574	128g/l	150	3	4x N2

Table 2.5: Parameters of the potassium pyrosulphate experiments performed.

2.4.1 Results and observations.

The reaction proceeded exothermic and the temperature peaked at 167°C while the controlling device was set at 150°C. At a temperature of 60°C the stirring rod was blocked and the reactants had formed a massive slurry, probably containing olivine, silica and
$K_2 Mg(SO_4)_2*6H_2O$ salt. No layers or otherwise separable phases were visible. It was obvious that the recipe had to be adjusted to lower concentrations.
It was found that both K_2SO_4 and $K_2 Mg(SO_4)_2*6H_2O$ are less soluble than potassium pyrosulphate. Therefore, for the second experiment the $K_2S_2O_7$ concentration was adapted to the solubility of K_2SO_4 and $K_2 Mg(SO_4)_2*6H_2O$. According to W. Voigt (2001) a 1,5 M of $K_2 Mg(SO_4)_2*6H_2O$ is completely soluble. To be on the safe side a 1M solution was used.
The third experiment was performed in order to measure the completion of the reaction. This time only 10 gr of olivine was added, theoretically enough to neutralize 0,13 moles of potassium pyrosulphate (assuming that the olivine is 90% mineralogical pure).

exp no	pH	filtrate	residue	silica	olivine consumed	Mg in sol.	remarks
		(gr)	(gr)	(gr)		(gr/l)	
6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	massive salt slurry
7	4,5	206,3	54,72	13,7	15%	13,80	heat development at start reaction
8	3,2	209,3	2,14	10,86	79%	12,31	heat development at start reaction

Table 2.6: Data of the reaction products formed from the olivine-potassium pyrosulphate reaction.

2.4.2 Discussion.

From experiment 7 can be concluded that the highest pH reached under 'moderate' reaction circumstances is pH 4,5. It further shows that the overall reactivity of potassium pyrosulphate is good, especially compared to acetic acid. Experiment 8 shows that either ± 20 % of the olivine product AFS 50 has not reacted. This means that either 20% of the product is not olivine or that the process at higher pH and decreasing availability of fresh olivine is slowed down in such a way that the reaction is not completed. According to Jonckbloedt (1997), more than 90 % of the commercial olivine should be pure olivine, for industrial application he uses a reaction percentage of 80 %.
From the experiments with pyrosulphate it is concluded that the final pH reached is not high enough for serious carbon dioxide precipitation.

2.5 Alkaline sodiumsulphate extraction of Mg^{2+} from olivine.

Another route to be investigated was a slightly alkaline route using a sodium sulphate solution for magnesium extraction:

eq. 2.3: $Mg_2SiO_4 (s) + Na_2SO_4 (aq) + H_2O \rightarrow Mg(OH)_2 (s) + MgSO_4 (aq) + Na_2SiO_3 (aq)$

This reaction has a slight positive)G (+78.3 kj/mole) and will not proceed spontaneously. Therefore the pH as increased by adding some 2,5 M NaOH. The advantages of these route could be:

- easy separation of $Mg(OH)_2$ by instantaneous precipitation at higher pH
- separation of SiO_2 by CO_2 addition
  $(Na_2SiO_3 (aq) + H_2O + 2CO_2 (g) \rightarrow SiO_2 (s) + 2NaHCO_3 (aq))$
- $MgCO_3$ precipitation and regeneration of Na_2SO_4 by $Mg(OH)_2$ addition
  $Mg(OH)_2 (s) + 2NaHCO_3 (aq) + MgSO_4 (aq) \rightarrow MgCO_3 + Na_2SO_4 (aq) + H_2O$

A higher reaction temperature was chosen than in previous experiments, because a slower reaction rate was expected.

exp no	date	olivine (gr)	Na_2SO_4 (gr)	water (gr)	pH in	NaOH 2,5 M	temp (°C)	duration
9	28-feb	21,01	42,09	282,2	11,54	1 ml	200	1,5 uur
10	1-mrt	21,45	42,8	281,45	11,92	2,5 ml	250	2 uur

Table 2.7: Parameters of the sodium sulphate experiments performed.

2.5.1 Results and observations.

After the reaction there was no instantly visible evidence for silica formed. The inside of the liner was etched. The contents of the liner were filtered and the residue was washed and dried. As can be seen in table 2.7 and 2.8 the residue almost equals the amount of olivine that entered the autoclave. After the filtrate had cooled down, two types of precipitate were formed, long transparent needles, presumably Na_2SO_4 and a cloudy white precipitate, probably some silica.

exp no	date	pH out	filtrate Ml	residu g
9	28-feb	8,96	320,5	20,4
10	1-mrt	11,38	322,29	20,24

Table 2.8: Data of the reaction products formed from the olivine-sodium sulphate reaction

2.5.2 Discussion.

Based upon the above reported results, this route offers no perspective on Mg^{2+} extraction from olivine.

3 MAGNESIUM EXTRACTION FROM SILICATES BY NITRIC ACID.

3.1 Introduction.

The earth alkaline extraction experiments were performed with concentrated nitric acid and a magnesium or calcium containing silicate, in this case olivine and anorthosite respectively. Purpose of the experiments with olivine was to obtain a general idea of the extraction processes and to produce material for the recovery of nitric acid and production of a magnesium component suitable for carbon dioxide sequestration. Experiments with anorthosite were performed only to compare the reaction rate of anorthosite to that of olivine.

3.2 Methods used.

Larger scale batch experiments using nitric acid and olivine have been performed in a double walled 1 litre glass reactor (see fig 3.1). The vessel was heated by an Lauda RM 30 circulating bath. Due to heat loss in tubes and the reactor itself the circulating bath temperature was set 4°C higher than the desired reaction temperature in the reactor.

Fig 3.1: Glass reactor from left to right at the beginning of extraction, at the end of extraction and at the end of experiment no 14.

The olivine was added at 15-20°C below the final reaction temperature so the reaction heat would help increase the reactor temperature, and perhaps more important, would exclude the risk of the reagents to boil. The reactor was stirred by an IKA rw 20.n motor and a glass stirring rod/impeller at 500 rpm. It was closely observed that all olivine was kept in suspension to prevent cementation to the wall or bottom of the reactor. The olivine was added stepwise in two or more doses within one hour to prevent this. At the end of the experiment the silica suspension was filtered on a büchner funnel using Schleicher & Schull GF6 glass fiber filters. The büchner funnel was connected to a flask with a tube leading to a Watson Marlow vacuum pump. In order to achieve the highest possible magnesium concentration in the effluent, the effluent was filtered at the highest possible temperature immediately after ending the reaction. Nevertheless crystallization was observed during the filtration of some suspensions. To prevent effluent crystallization the büchner funnel was placed in a stove at 90°C prior to filtration.

The residue in the reactor was washed with tap water, shaken and immediately decanted in order to separate the last silica from the non reactive parts of the olivine. This water was added to the silica filter cake in the büchner funnel. Both the residue and the silica were dried in an oven at 90°C and subsequently weighed. The effluent was analysed on density, pH and percentage of crystals formed at room temperature.

3.3 Theoretical background of olivine dissolution in acid

In nature the weathering of silicates is one of the means by which acidity is controlled. Silicates consist of a network of silica tetrahedra (SiO_4^{4-}), which are balanced by cations (Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, Na^+, K^+). In aluminosilicates part of the silica is replaced by alumina. Upon weathering the cations and alumina are leached from the structure and a H_4SiO_4 skeleton is formed. As a rule of thumb the vulnerability of the silicates to weathering depends on the silica/cation ratio. With increasing silica content, there will be too little cations to balance the silica and the silica tetrahedra will be more and more inter connected by sharing oxygen atoms. The result is that silica tetrahedra can form chains, double chains and sheets between which the cations are situated. The more oxygen atoms are shared by silica tetrahedra, the more resistant the silicate will be. These varying silica structures make that some silicates dissolve congruently and others release their cations and alumina first or at a higher rate. Olivine has no oxygen sharing silica tetrahedra and is known to dissolve congruently. The way plagioclase dissolves is depending on the anorthite percentage, pure anorthite dissolves congruently whereas albite first releases its cat ions, leaving a silica framework behind.

Under natural circumstances in both cases a silica layer will be formed on the mineral surface. If the mineral dissolves congruently this layer is newly formed by precipitating silica, in case of incongruent solution this layer is residual. Precipitation of silica can be avoided by mutual attrition of the grains by stirring the suspension. The dissolution of olivine and anorthosite in nitric acid is given in the following equation:

eq. 3.1: $$4\ H^+ (aq) + NO_3^- (aq) + (Mg,Fe)_2SiO_4 (s) \rightarrow 2\ Mg^{2+} (aq) + 4\ NO_3^- (aq) + H_4SiO_4 (s)$$

eq. 3.2: $$9.2\ H^+ (aq) + NO_3^- (aq) + (Ca_{0.7},Na_{0.3})Al_{1.7}Si_{2.3}O_8 (s) \rightarrow$$
$$0.7\ Ca^{2+} (aq) + 0.3\ Na^+ (aq) + 1.7\ Al^{3+} (aq) + 9.2\ NO_3^- (aq) + 2.3\ H_4SiO_4 (s)$$

When the dissolution proceeds the amount of dissolved silica increases until it is supersaturated (0,05 mol/l, D. Lieftink) and starts to form chains within the liquid. These chains greatly influence the viscosity of the reaction mixture and while the reaction is proceeding the viscosity increases. The onset and duration of this viscosity phase depends on the grain size of the olivine and the reaction temperature. At higher temperatures and smaller grain sizes the onset is earlier and the phase lasts shorter. When performing high concentration experiments this viscosity can seriously hamper the process. If the turbulence in the reactor is diminished due to viscosity increase, larger olivine particles will settle and cement to the reactor.

Magnesium nitrate occurs in a dihydrate, hexahydrate and a nonahydrate form and is highly soluble (up to 125 gr/l for magnesium hexahydrate). The hexahydrate form melts at 90°C or more precisely dissolves in its own crystal water. Between 50°C and 90°C magnesium nitrate exhibits three different solubilities as can be seen in fig 3.2. No literature was found on the solubility of mixed Fe(II) and Mg nitrates.

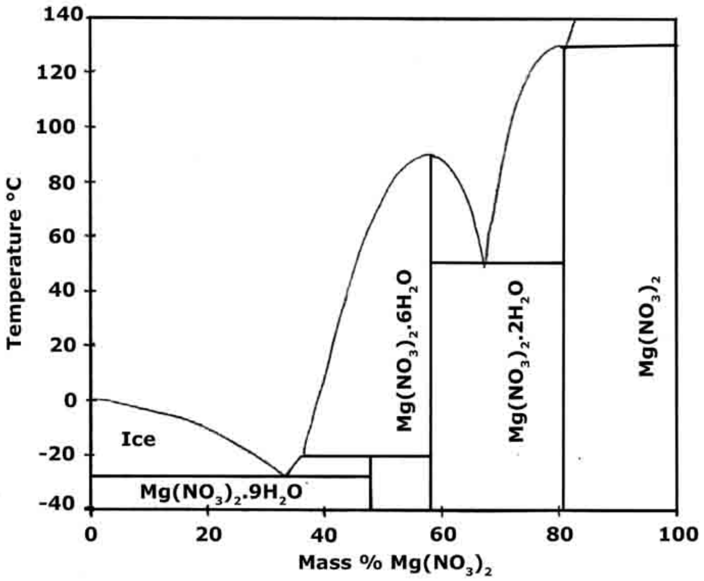

Fig 3.2: The magnesium nitrate-water binary system (K.Thomsen, Aqueous Solutions, Denmark)

3.4 Experimental approach

Calculation of experimental recipes for olivine neutralization in nitric acid.

Starting point for the magnesium extraction experiments is the solubility of $Mg(NO_3)_2.6H_2O$ which is 1,25 kg/l. To obtain an extract chemically close to this concentration the following calculation is made.
The density of $Mg(NO_3)_2.6H_2O$ is 1,64 kg/l so 1,25 kg magnesium nitrate equals 0,76 l and for the maximum concentration in solution another 0,24 l H_2O has to be added. In solution we now have 0,72 kg $Mg(NO_3)_2$ and 0,76 kg H_2O. The Mg is derived from the olivine for which we have to solve 0,40 kg olivine (corrected for the iron content and inert material). The nitrate is derived from the nitric acid of which 0,61 kg is needed, or 0,88 kg HNO_3 70%. To complete the solution 0,76 kg - 0,27 kg (from the nitric acid) = 0,49 kg H_2O is needed.

According to Jonckbloedt (1997) the olivine used for these experiments, AS Olivin AFS 50, contains 94,8% olivine and 5,2% inert material. One mole of olivine consumes four moles of HNO_3. The molar weight of the olivine is 145,1 g. So 100 gr AFS 50 ~ 94,8 gr olivine ~ 0,65 mol olivine ~ 2,61 mol HNO_3 ~ 165 gr HNO_3 ~ 235 gr HNO_3 70% w/w.

The theoretically ideal recipe for a saturated magnesium nitrate solution then would be:

1	kg olivine
2,2	kg nitric acid 70%
1,25	kg water

For the experiments a few conditions were set. The process has to be robust and applicable on an industrial scale. Therefore the overall reaction time has to be within reasonable boundaries and the loss of energy minimal.

Temperature is one of the key parameters for reaction kinetics of olivine dissolution. At low temperature (40°C) the extraction will take several days to completion, at higher temperatures (80°C) this is reduced to a few hours. Reaction time could be even reduced to less then an hour, but this would imply the use of an autoclave and related vulnerable pressure equipment. The process itself is exothermic which results in a significant temperature increase after olivine has been added.

Another important parameter is concentration of the reactants. Although the olivine neutralization process could go on beyond pH 7, the reaction rate will fall progressively with decreasing H^+ activity. The same goes for the amount of fresh olivine available for the reaction. The third parameter is grain size of the olivine. There is a linear relation between the olivine dissolution rate and the surface area of the olivine grains.

Temperature

The temperature was chosen to be 80°C except for the first HNO_3 experiment (no 11) which was performed at 60°C and experiment no 14 which was performed at 90°C in order to keep all dissolved reactants in solution.

Reaction time

The reaction time varied between two and five hours

Reaction concentrations

The aim for total reagent consumption was set at 80% olivine and 90% HNO_3.

Olivine grain size.

The olivine used was AFS 50 from AS Olivine and supplied by Holland Mineraal BV. According to specifications from the supplier, the grain size fraction would be 0,1-0,3 mm. Analyses supplied by TNO MEP revealed that this was 0,1-0,7 mm.

3.5 Results

3.5.1 Description of experiments

In table 3.1 the experimental parameters of all nitric acid earth alkaline element extraction experiments are given.

	date	H2O (gr)	HNO3 70% (gr)	olivine (gr)	t (min)	T (°C)	number olivine addition steps	interval between ol. add. (min)
exp 11	9-3-05	311	518	200	280	60	2	60
exp 12	30-3-05	312	519	200	240	80	2	60
exp 13	15-11-05	280	540	235	250	77	2	60
exp 14	20-12-05	85	769	340	160	90	3	30
exp 15	21-12-06	280	538	235	300	80	2	30
exp 16	30-1-06	280	537	235	232	77	4	20
exp 17	31-1-06	281	538	235	240	77	4	15
exp 18	3-2-06	279	542	252	240	80	4	15
exp 19	6-2-06	280	541	251	112	80	4	15
exp 20	8-2-06	281	540	250	210	80	4	15
exp 21	10-2-06	281	541	250	240	80	4	15
exp 22	26-6-06	500	100	219	480	79	1	
exp 23	28-6-06	500	101	222	480	78	1	
exp 24	4-7-06	500	100	221	480	78	1	
exp 25	6-7-06	190	655	290	360	89	3	20
exp 26	10-7-06	501	100	501	480	77	1	

Tabel 3.1: Experimental data of the nitric acid extraction experiments

Below follows a brief description of the specific of each experiment:

Experiment 11. The first HNO_3 experiment was basically a try-out to get empirical insight in the reaction between olivine and nitric acid, therefore the reaction temperature chosen was relatively low and the amount of olivine sub stoechiometrical. Olivine was added until it was no longer kept in suspension. The initially green-grey suspension turned viscous and yellow after approximately 30 minutes. Yellow-brown fumes appeared above the suspensions surface. The remaining olivine was added after one hour, after which the experiment ran for another 2 hours and 40 minutes.
The suspension was decanted and immediately filtrated. The first filtration attempt failed when the filter paper was completely digested by the suspension. A second attempt was done three days later using glass fibre filters. After cooling crystals formed in the filtrate. Some of the olivine was cemented to the reactor bottom.

Experiment 12 was identical to 11 except for the reaction temperature which was 80°C and the reaction time of 4 hours.

Experiment 13: more olivine and nitric acid where used in order to produce a more concentrated Mg filtrate.

Experiment 14: One of the disadvantages of the HCl extraction route is the energy needed for crystal water decomposition in various steps. $Mg(NO_3)_2$ *exhibits three different solubilities between 50°C and 90°C with an eutectic point at 50°C and a chemical solution composition that equals* $Mg(NO_3)_2.4H_2O$*. Therefore one reaction mixture which would yield this filtrate was calculated and used. The effect that* $Fe^{2+/3+}$ *could have on the solubility of the reaction product was unknown. The olivine was added in three steps, the first one was already added at 70°C to speed up reactor heating. The viscosity already increased after 6 minutes. The suspension quickly turned dark brown and thick brown fumes where forming in the top part of the reactor. At the end of the experiment the suspension was stirred at slow speed in order to help settling of the residue. The slurry was decanted in a beaker and immediately transferred to the filter which was placed in an oven at 90°C. Filtration proceeded slowly and a brown clear syrup like filtrate was obtained. The remaining slurry immediately crystallized on the beaker wall and was very hard to remove. After filtration the silica cake and filtrate cooled down and solidified. The dark brown filtrate turned red upon reheating. The filter cake was hard and very difficult to resolve.*

Experiment 15 to 17: Comparable to experiment 13 but with slight variations in experiment duration.

Experiment 18: Increase of olivine in order to obtain more concentrated filtrates. The magnesium nitrate content of the slurry already started crystallizing during filtration. Deviates from experiment 19 to 21 only for the fact that the büchner filter was not preheated.

Experiment 19 to 21: Same condition as for experiment 18 only varying in experiment duration. For silica filtration a preheated büchner filter was used. In this series filtration of experiment 19 was the most difficult. It was generally observed that there is a positive correlation between experiment duration, concentration of the reagents and filterability.

Experiment 25: Experiment with a recipe that would, according to figure3.2, result in the least soluble magnesium nitrate liquid. However, compared to experiment 14 no remarkable differences in solubility and crystallization were observed. Upon adding cold rinsing water the filter cake immediately solidified like in experiment 14. It is assumed that this will not happen when using hot tap water. The filter cake was left for one night with a layer of water on top. Next day all water had trickled through and the filter cake had become soft. Compared to experiments 19, 22, 23, 24 and 26 filtration proceeded relatively quickly.

Experiment 22, 23, 24 and 26: Experiments performed for reaction rate comparison of anorthosite and olivine in nitric acid. Filtration of the silica was troublesome in all experiments. The experiments carried out on anorthosite were all practically non filtrable.

3.5.2 Description of reaction products from Mg extraction from olivine by nitric acid.

Physical data on the reaction products formed during the olivine dissolution in nitric acid are given in the table 3.2.

	residue (gr)	silica (gr)	silica calc. (gr)	silica DM %	filtrate (gr)	crystals (gr)	total (gr)	% krist	density filtrate g/ml	residue/ olivine
exp 11	57	50	61	n.d.					n.d.	0,28
exp 12	36	70	70	n.d.	574	99	673	14,7%	n.d.	0,18
exp 13	52	78	78	n.d.	320	254	574	44,3%	n.d.	0,22
exp 14	83	142	110	n.d.				100,0%	n.d.	0,24
exp 15	52	81	78	n.d.	360	316	676	46,7%	1,397	0,22
exp 16	58	79	76	n.d.	311	339	650	52,2%	1,398	0,25
exp 17	56	74	77	n.d.	396	285	681	41,9%	1,398	0,24
exp 18	63	77	81	n.d.	347	277	624	44,4%	1,402	0,25
exp 19	103	68	63	0,38	445	137	582	23,6%	1,386	0,41
exp 20	64	84	80	0,41	403	257	660	38,9%	1,405	0,26
exp 21	52	83	80	0,42	288	358	646	55,4%	1,413	0,21
exp 22	19	96	35	n.d	n.d	n.d	n.d	0 %	n.d	0,19
exp 23	83	6	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
exp 24	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
exp 25	65	133	96	0,41				100,0%	n.d	0,22
exp 26	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d

Table 3.2: Description of reaction products from Mg extraction from olivine by nitric acid

Immediately after filtration the colour of the nitrate solutions is brown. Upon cooling crystals start to form and the colour of the liquid shifts to green. When reheating the filtrate, the brown colour reappears. The filtrate of experiment 14 totally solidified and remained brown. In order to remove the filtrate from the suction flask it was reheated and turned Bordeaux red. Of the greater part of the filtrates density and the amount of crystallization was determined. Of the filtrates from experiment 15 to 21 dilutions were made which were analyzed at the TNO laboratory in Utrecht. TGA and ICP-MS were carried out on the filtrate of experiment 14. The analytical results are given in table 3.3.

name	Mg (g/kg)	Fe (g/kg)	Ni (g/kg)	Mn (g/kg)	Al (g/kg)	K (g/kg)	Na (g/kg)	Ca (g/kg)	Co (g/kg)	Fe/Mg
Ext 14	84,30	17,52	1,17	0,31	0,16	0,09	0,03	0,06	0,05	0,208
Ext 15	52,23	9,14	0,54	0,14	0,07	0,06	0,04	0,03	0,02	0,175
Ext 16	53,00	9,06	0,55	0,14	0,07	0,08	0,08	0,03	0,02	0,171
Ext 17	54,76	9,27	0,55	0,14	0,07	0,07	0,04	0,03	0,02	0,169
Ext 18	56,11	11,16	0,63	0,17	0,09	0,08	0,05	0,04	0,03	0,199
Ext 19	45,76	7,55	0,44	0,11	0,07	0,05	0,03	0,03	0,02	0,165
Ext 20	60,37	10,29	0,59	0,16	0,10	0,06	0,04	0,03	0,03	0,170
Ext 21	64,79	10,64	0,62	0,16	0,10	0,06	0,04	0,03	0,03	0,164
Ext 18-kr	43,19	10,91	0,45	0,15	0,09				0,02	0,253

Table 3.3: ICP analysis of the magnesium extracts from experiment 14 to 21

The data show that the extracts are relatively pure Mg-Fe solutions with Ni as most important minor pollutant. Ratios of Fe, Ni, Mn and Al are given in figure 3.3. The ratio of Fe to Mg in the filtrates ranges from 0,164 to 0,253. Ext 18 and 14 show increased Fe/Mg ratios probably due to partial crystallization of magnesium nitrate during filtration. The highest Fe/Mg ratio is achieved in the remaining solution of ext 18 after removal of the magnesium nitrate crystals. Ni and Mn, however, do not follow the same trend as Fe and decrease in Ext 14.

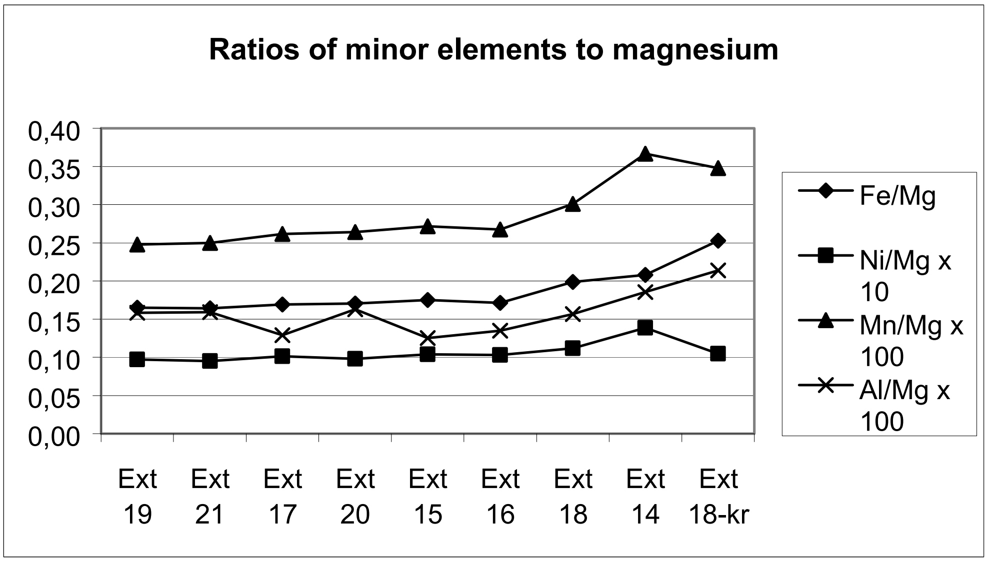

Figure 3.3: Ratios of various elements in the Mg extract/Mg

If the density of the filtrates is plotted against the Mg content (fig 3.4) a good correlation is visible, measuring the density of the filtrate could therefore be a useful tool in makeshift Mg determinations in an eventual extraction plant.

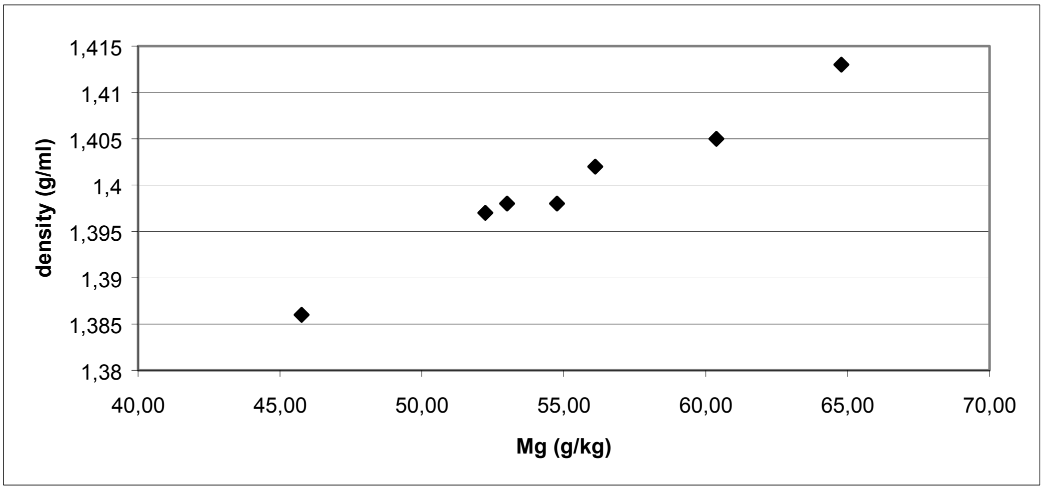

Figure 3.4: Density of magnesium extract plotted against Mg concentration.

3.6 Interpretation of reaction products and observations from Mg extraction from olivine by nitric acid.

In order to avoid energy spill by evaporation of redundant water during the recovery of nitric acid, the experiments were aiming at the highest possible magnesium nitrate concentration. For the calculation of the reagents the maximum solubility of $Mg(NO_3)_2.6H_2O$ was taken as a starting point, however, the presence of iron and other metals in the final filtrate was not taken into account. The first experiment (exp 11) was, regarding the expected Mg extraction, performed with reagent quantities theoretically resulting in a sub-saturated magnesium nitrate solution. Nevertheless, after the filtrate had cooled down to room temperature crystals had formed. If we look at the analyses of experiment 19, having the lowest Mg concentration, and we recalculate the Mg and Fe content to the respective nitrate salts, this will be 676,4 and 38,9 gr/l. The total of these amounts is even well below the solubility of $Fe(NO_3)_2.6H_2O$, which is 835 g/l. Still in this filtrate 23,6 % of the total mass crystallised. It can be concluded that the solubility of magnesium nitrate in presence of other metals in solution is greatly reduced.

One other objective, the extraction at 90°C using the lowest possible amount of water as carried out in experiment 14, gave, when recalculating the ICP data to their respective salts, the result as given in table 3.4.

MgO	Fe_2O_3	NiO	MnO	Al_2O_3	total oxides	LOI	total
13,98%	2,51%	0,15%	0,04%	0,03%	16,7%	82,9%	99,6%
$Mg(NO_3)_2.4H_2O$	$Fe(NO_3)_3.9H_2O$	$Ni(NO_3)_2.6H_2O$	$Mn(NO_3)_2.6H_2O$	$Al(NO_3)_3.9H_2O$			
76,40%	12,67%	0,58%	0,16%	0,22%			90,0%
$Mg(NO_3)_2.6H_2O$	$Fe(NO_3)_3.9H_2O$	$Ni(NO_3)_2.6H_2O$	$Mn(NO_3)_2.6H_2O$	$Al(NO_3)_3.9H_2O$			
88,88%	12,67%	0,58%	0,16%	0,22%			102,5%

Tabel 3.4: Recalculation of all oxides of exp 14 to corresponding nitrates

As already mentioned in paragraph 3.5.1 the recipe for the reagents used in experiment 14 was calculated in order to produce a magnesium nitrate extract that would chemically equal $Mg(NO_3)_2.4H_2O$. If we recalculate the results from the ICP-MS to 1) the magnesium nitrate we aimed to produce and 2) to the nitrate that is stable at room temperature, we find out that the TGA and ICP analyses are much closer to the latter one. This is probably because (as calculated from the residue left) only 257 gr of olivine was consumed in the process whereas 300 should have been consumed to obtain the desired nitrate composition. This means that in the end there was still too much water available. Another additional factor could be is that the reaction mixture itself is highly hygroscopic. It was observed that the solidified filtrate did sweat and fume, while spreading a pungent odour.

It was observed that both reaction time and concentration of the reagents influences the filterability of the reaction products. In the sub-series of experiments 19,20 and 21, experiment 19, having the shortest reaction time of only 112 minutes, turned out to be the hardest to filter. Even more troublesome were the experiments were the lowest concentrations reagents were used (experiments 22, 23, 24 and 26). The filtration of the silica from experiment 22 took several hours and was stopped during the night, the following morning the remaining suspension in the filter had taken a jelly like appearance and was not filterable anymore. The decanted suspensions from the anorthosite experiments were likewise difficult to filter. Besides the fact that no distinction could be made between silica and very fine grained anorthosite, the suspension from the fine grained anorthosite reaction turned out to be non-filterable.

The Fe/Mg ratio of the filtrates from experiments 18 and 14 significantly deviates from the Fe/Mg ratio of other filtrates. Whereas most Fe/Mg ratios of the filtrates hover around 0,17, the above mentioned filtrates have ratios around 0,20. What these experiments have in common, is that their filtrates already visibly started to crystallize during filtration of the silica. It can be assumed that during this crystallization a chemical fractionation has taken place which resulted in a filtrate that was enriched in Fe. This assumption is confirmed by a comparing titration experiment for which two solutions were used: One dilution made from warm (60°C) extraction filtrate and another made from cold (20°C) extraction fluid from which the precipitated magnesium nitrate crystals were removed. The titration curves are given in figure 3.5.

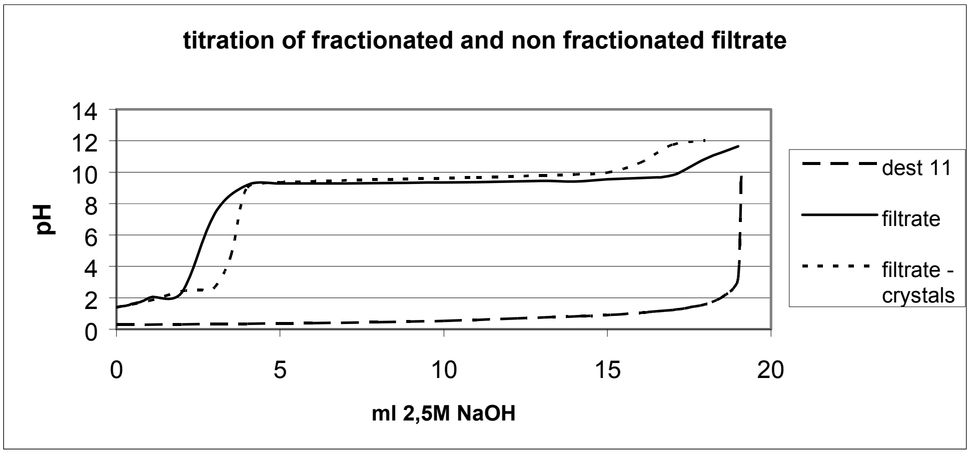

Fig 3.5: Titration curves of distilled nitric acid, magnesium nitrate extract and magnesium nitrate extract minus fractionated crystals.

In this figure it is clearly visible that by removing the crystals from the magnesium extract the buffering capacity around pH 2-3 of the remaining liquid is increased. On the other side the buffering capacity around 9-10 is decreased. This is caused by the selective removal of Mg and corresponding accumulation of Fe in the remaining liquid.
ICP analysis of the fractionated magnesium nitrate filtrate does show an increased Fe/Mg ratio. However, it does not show a absolute increase of the Fe, Ni and Mn content as would be expected from the titration results and experiments 14 and 18.
It is likely that by carefully adding $MgCl_2$ to the remaining liquid, more magnesium nitrate crystals can be separated from a residual iron salt solution. This has not been investigated yet.

4 COMPARISON OF THE REACTION RATE OF ANORTHOSITE TO THAT OF OLIVINE.

4.1 Introduction

Plagioclase is a calcium/sodium silicate with a composition varying from $NaAlSi_3O_8$ (pure albite) to $CaAl_2Si_2O_8$ (pure anorthite). According to research by Stillings and Brantley (1995) pure anorthite exhibits a dissolution rate comparable to that of olivine. Although calcic plagioclase contains less components suitable for carbon dioxide sequestration (only 19 wt% of CaO whereas olivine contains 56 wt% of MgO), calcic plagioclase could be useful in industrialized areas where it is abundant in highly concentrated easily accessible depositions. The reactivity of plagioclase quickly drops with increasing amount of sodium.

Experiments were conducted on order to compare the actual dissolution rate of commercially available anorthosite and olivine. The same olivine was used as for the other extraction experiments. The anorthosite sample plus analytical information was obtained from Gudvangen Stein AS at Voss, Norway. The average composition of the anorthosite is given in table 4.1.

SiO2	49,48	Na2O	2,93
Al2O3	30,64	K2O	0,22
Fe2O3	0,73	MnO	0,006
TiO2	0,1	P2O5	0,11
MgO	0,42	LOI	0,97
CaO	14,21	Sum	99,80

Table 4.1: Average chemical composition of the Gudvangen Stein Anorthosite

This corresponds to an chemical formula of $(K_{0.01}\ Na_{0.26}\ Ca_{0.71})(Al_{1.67}\ Fe_{0.03}\ Si_{2.29})O_8$ and an anorthite percentage of ± 70%. Based on this anorthite percentage the minerals in this rock would classify as a labradorite/bytownite. Note that the rock name anorthosite is used for a rock containing calcic plagioclase and not for a rock consisting of pure anorthite. The anorthosite sample was sieved in the following fractions: <105µ, 105µ<x<1mm and >1mm.

4.2 Method used.

The four experiments were performed at the same temperature as the other extraction experiments, smaller amounts of reagent were used in order to lower the reaction rate. Two of the anorthosite experiments were performed using a grain size fraction of 110 µ to 1 mm, one experiment was performed with the < 110µ fraction. Samples of 6-10 ml were taken at intervals of 15,30, 60 and 120 minutes depending on the expected rate of the reaction. The duration of the extraction experiments was 6 hours. The samples were left to settle as far as possible and a 2,5 ml sub-sample was taken and diluted with 100 ml water. The diluted sample was titrated with a 1,25 molar NaOH solution until neutral and the pH was measured.

After the experiment the contents of the reactor were decanted and the suspension was filtered. Filtration was very slow for the olivine experiment and extremely slow for the anorthosite experiments. Due to the fine grain size the separation of silica from the fine anorthosite (<105µ) turned out to be impossible.

4.3 Results and observations.

The percentage of acid converted to (earth)alkaline ions in time of three of the experiments is given are given in table 4.2. This percentage is based on the amount of NaOH needed to reach pH 7 for each sample divided by the total NaOH needed to neutralize the original nitric acid. It is assumed that only earth alkaline ions are in solution above this pH. The titration of the samples taken from the olivine experiment proceeded according to expectations. The pH of al diluted sub samples was increasing linearly and the amount of NaOH needed for neutralization was decreasing hyperbolical with time.

During the titration of the anorthosite samples some irregularities occurred. First of all the pH of the diluted sub samples showed erratic behaviour. For some samples taken in course of the experiment the pH of the diluted sub-sample was lower than the pH of the likewise diluted nitric acid used for the experiments (see fig 4.1). Second, some samples required less NaOH for neutralization than would be expected based on their number in the sampling sequences (see the sample taken at 63 min from the coarse anorthosite experiment). Some samples taken from the fine anorthosite experiment were left overnight for titration, however, the following day pH measurements indicated that the neutralization had continued. Therefore only samples that were titrated immediately after sampling were used for interpretation.

anorthosite fine (exp 24)		anorthosite coarse (exp 26)		olivine (exp 22)	
t (min)	conversion	t (min)	conversion	t (min)	conversion
0	0,00%	0	0,00%	0	0,00%
7	2,60%	63	12,10%	4	4,20%
197	6,20%	123	5,40%	19	20,10%
245	10,10%	245	11,60%	63	55,00%
		353	11,40%	92	61,20%
				153	70,80%
				214	79,30%
				274	83,30%
				365	87,50%

Table 4.2: Percentage of acid converted to earth alkaline ions (Na, Mg, Ca)

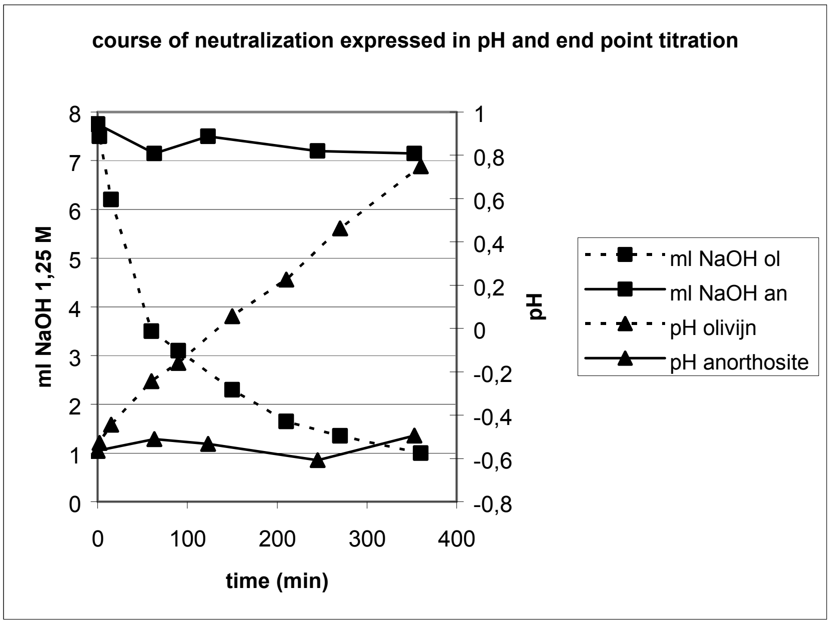

Figure 4.1: pH (recalculated) and NaOH consumption of the magnesium nitrate samples taken in experiment 22 and 26.

4.4 Interpretation.

At first glance it is clear that the extraction of earthalkaline ions from olivine is 8 to10 times more effective than extraction from the anorthosite sample used for these experiments. If we take into account that a considerable part of these ions is sodium and therefore irrelevant for the sequestration of carbon, this ratio is even worse.

The data from the anorthosite experiment show some remarkable deviations compared to the data from the olivine experiment. The pH drop of the diluted samples to values even below the starting value and the shift of endpoint of the sample taken at 63 min of the coarse anorthosite experiment. In these cases it is very probable that we are looking at phenomena induced by the dilution of the samples.

The shift of endpoint can be caused by incongruent dissolution of the anorthosite (Stillings L.L. and Brantley S.L., 1995), which means that in the beginning of the reaction Na and Ca are preferentially leached. When the outer zones of the plagioclase are depleted of Ca, Si and Al start to go into solution. However, since the titration endpoint shifts back, Ca has to disappear again to make the hypothesis work. Altogether, the extraction of Ca from anorthosite seems to results in a suspension that exhibits a changing stability due to varying levels of cations in solution. This anorthosite option could be further developed if there exists a way to selectively leach Ca. If not, this route is highly unfavourable compared to the olivine route.

5 HNO_3 REGENERATION BY THERMAL DECOMPOSITION OF $Mg(NO_3).6H_2O$.

5.1 Introduction

Hydrochloric acid has been considered as one of the options to extract magnesium from olivine for the sequestration of carbon dioxide. For the recovery of $Mg(OH)_2$, $MgCl_2.6H_2O$ has to be decomposed and hydrochloric acid and a considerable amount of water has to be evaporated. This is done in a two step process during which additional water has to be added to separate $Mg(OH)_2$ from the Mg(OH)Cl which is formed during the first step.

Compared to the above mentioned extraction route nitric acid extraction has the advantage of forming hydrated magnesium nitrate from which MgO or $Mg(OH)_2$ can possibly be recovered in one step. In this research experiments were performed that show the possibility of nitric acid recycling. Further one attempt was made to perform simultaneous nitric acid recovery and carbon dioxide sequestration.

5.2 Methods used.

Magnesium nitrate thermal decomposition was performed in two coupled autoclaves, one 600 ml Parr 4560 autoclave (carpenter alloy 20Cb-3) and the other a two litre titanium Parr 4520 autoclave (fig 5.1). The autoclaves were connected by a 1m 316L SS tube. The smaller autoclave served as a decomposition chamber and the bigger autoclave served as a condensation chamber. The smaller autoclave was heated in a 780 watt heating mantle and controlled by a Parr 4842 console. Magnesium nitrate crystals or solution were weighed in a glass liner, the liner was placed in the autoclave. An empty liner was weighed and placed in the bigger autoclave. The small autoclave was heated at slow rate to a temperatures between 320 and 340°C. During some experiments the connecting tube and bigger autoclave were water or ice cooled.

Experimental data are given in table 5.1. In three experiments carbon dioxide was added. All decomposition experiments are carried out near the guaranteed safety limits of the autoclave. The synthesis of magnesite is an exothermic reaction. Therefore, the temperature of the first run under carbon dioxide atmosphere (dest 4) was carefully manually increased to minimize the chance that uncontrollable situations would occur. After the decomposition the autoclave was air cooled to room temperature. The autoclaves were opened and the contents weighed. The density of the regenerated nitric acid was measured and of four condensates the nitric acid content was determined by titration.

Nitric acid is very aggressive and this has caused some leakage problems during some of the experiments. The autoclave main parts which were made of carpenter 20Cb-3 alloy turned out to be very resistant to the hot nitric fumes. The smaller parts like connecting tubes and sealing rings were less resistant. Especially the silver bomb head gasket had to be replaced frequently. Erosion of the gasket was most severe during experiments that were carried out under carbon dioxide pressure. In order to achieve a longer lifecycle for the silver gaskets the initial amount of 200 grams of sample for decomposition was reduced to 100 grams per experiment.

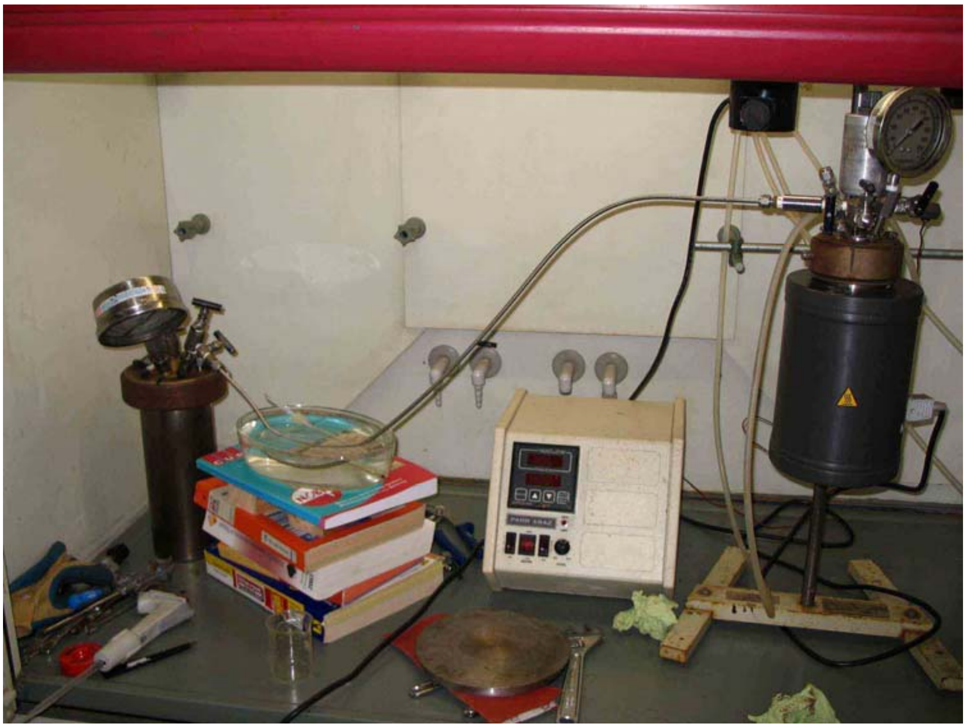

Figure 5.1: Magnesium nitrate decomposition set up. From left to right: condensation vessel, water/ice cooling, temperature console and decomposition autoclave.

	used	From	MgNO3 (g)	pCO_2 (bar)	T> 320 (min)	
dest 1	liquid (60°C)	exp 13	201,8		8	Connecting tube water cooled
dest 2	liquid (60°C)	exp 13	200,9		173	Connecting tube water cooled
dest 3	crystals	exp 12	100,2		69	
dest 4	liquid (60°C)	exp 21	198,8	5,0	42	
dest 5	liquid (60°C)	exp 18	100,9	2,2	72	
dest 6	liquid (60°C)	exp 18	100,6	2,0	69	
dest7	liquid (60°C)	exp 18	100,3		20	
dest 8	crystals	blend	100,2		34	
dest 9	crystals	blend	101,0		47	tube and reservoir ice cooled
dest 10	crystals	blend	100,6		30	tube and reservoir water cooled
dest 11	crystals	blend	100,9		70	Connecting tube ice cooled

Table 5.1: General experimental data of the decomposition/destillation experiments.

5.3 Theoretical background of magnesium nitrate decomposition.

According to the Handbook of Chemistry and Physics magnesium nitrate hexahydrate decomposes at 330°C. Mu and Perlmutter (1981) have performed TGA experiments at 1°C/min and give ranges for the decomposition of $Mg(NO_3).6H_2O$ (48-285°C), $Mg(NO_3)$ (290-410°C) and MgO (>450°C) respectively. Gardner and Messing have demonstrated that the start of decomposition in TGA depends on the rate of heating, TGA analyses at 10°C/min and 100°C/min gave decomposition temperatures of 450°C and 490°C respectively.

However, more recent studies indicate that the decomposition of hydrated magnesium nitrate is probably more complex than simple dehydration followed by decomposition of the nitrate groups. In magnesium nitrate hexahydrate the Mg atoms are six-fold coordinated to the water molecules yielding a distorted octahedra. The nitroxid-group is chelating these aqueous Mg complexes by introducing hydrogen bridges to the hydrogen atoms of the water molecules (Schefer and Grube 1995). This structure very probably inhibits the complete dehydration of magnesium nitrate hexahydrate without breaking the structure and losing some nitrate groups at the same time. Malecki et al. (2000) have done experimental research on several 4d-metal nitrates hydrates and concluded that the decomposition of metal nitrate hydrates proceeds in three stages:

1. $M(NO_3)_2.6H_2O \rightarrow M(NO_3)_2.(6\text{-}x)\ H_2O + xH_2O$
2. $M(NO_3)_2.(6\text{-}x)H_2O \rightarrow M(OH)_r\ (NO_3)_{2-r} + rHNO_3 + (6\text{-}x\text{-}r)H_2O$
3. $M(OH)_r\ (NO_3)_{2-r} \rightarrow MO + aNO + bNO_2 + cO_2 + r/2\ H_2O$

This implicates that no intermediate anhydrous magnesium nitrates are formed during decomposition. In contradiction with step three Styris and Redfield observed that hydrated magnesium nitrate decomposes with the formation of $Mg(OH)_2$ molecules. This implies that somewhere during stage two all nitrate is already lost before all water has been removed. Other studies (Gadalla and Yu, 1990) show that the type of intermediate products formed strongly depends on the atmosphere in which the decomposition is performed (vacuum, stagnant air, flowing air, nitrogen).

5.4 Results and observations.

During the experiments two stages of decomposition could be observed: the first being the dehydration stage roughly between 120-150°C and the second being the nitrate decomposition stage beginning at ± 320°C. Transport of the decomposition gases of these stages could be detected by temperature increase of the stainless steel connecting tube. The temperature curves from the experiments vary considerably in shape and range from smooth (exp 2,4,9) to frayed with sudden relapses and increases (exp 3,8). A few curves (exp 3,7,8,11) peak to 350°C before stabilizing around 330-340°C. Two curves are given for example in figure 5.2. The experiments carried out with 200 ml solution needed approximately 35 minutes longer to reach the aimed decomposition temperature. As mentioned in paragraph 5.2 the curve for dest 4 strongly deviates.

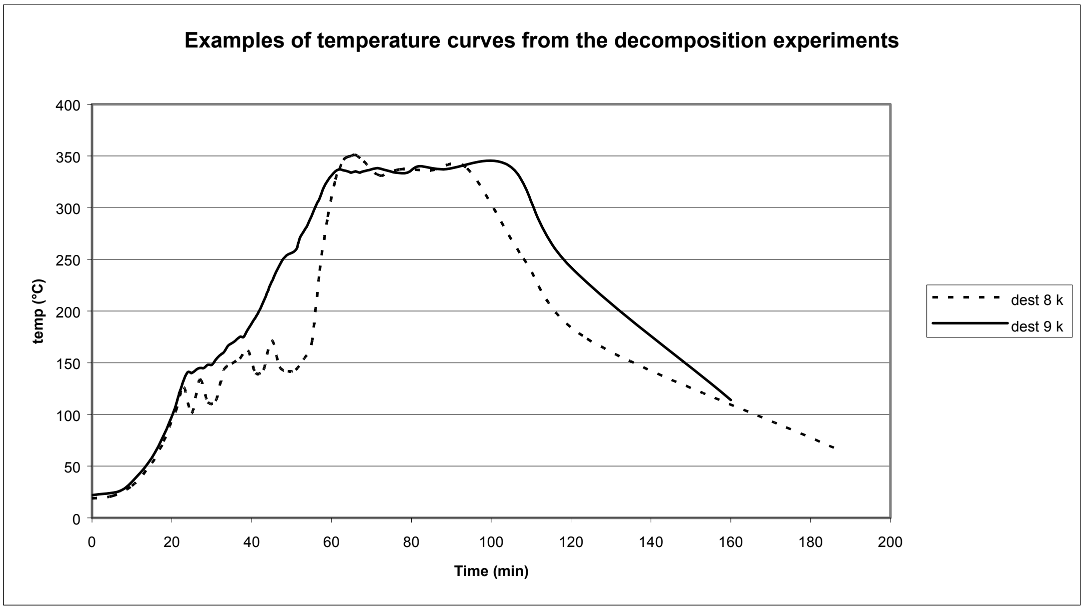

Figure 5.2: Examples of temperature curves of decomposition experiments.

	used	residue (g)	destillate (g)	spill (g)	residu/ input	T> 320°C (min)	T max (°C)	acid density	
dest 1	liquid (60°C)	78,8	110,5	12,5	0,39	8	325	1,08	L
dest 2	liquid (60°C)	34,8	161,5	4,6	0,17	173	335	1,23	L
dest 3	crystals	26,6	69,4	4,2	0,27	69	333	1,26	L
dest 4	liquid (60°C)	44,8	142,4	11,6	0,23	42	320-346	1,23	
dest 5	liquid (60°C)	26,9	70,1	3,9	0,27	72	330	1,18	
dest 6	liquid (60°C)	24,0	70,3	6,3	0,24	69	340	1,20	l at end
dest7	liquid (60°C)	31,7	69,0	-0,4	0,32	20	337	1,16	
dest 8	crystals	33,8	45,9	20,5	0,34	34	337	1,26	l at 240°C
dest 9	crystals	34,5	65,8	0,7	0,34	47	338	1,25	
dest 10	crystals	38,3	60,0	2,3	0,38	30	338	1,21	
dest 11	crystals	25,5	74,7	0,8	0,25	70	339	1,28	

Table 5.2: data of residue and distillate of decomposition experiments l = leakage

As intended, in all experiments the decomposition fumes had flowed towards the bigger autoclave and formed condensates. The nitric acid collected in the larger autoclave is fuming and colourless, a small amount of nitric acid remained in the connecting tube between the small and had turned green, probably due to nickel from the stainless steel connecting tube having gone into solution.

The nitric acid was collected and weighed. Its density was determined by weighing a 5 ml sub sample. From experiments dest 1, 2, 3 and 11 a 5 ml nitric acid sample was taken and diluted, after which pH measurement and end point titration were performed. The results are given in Fig 5.3.

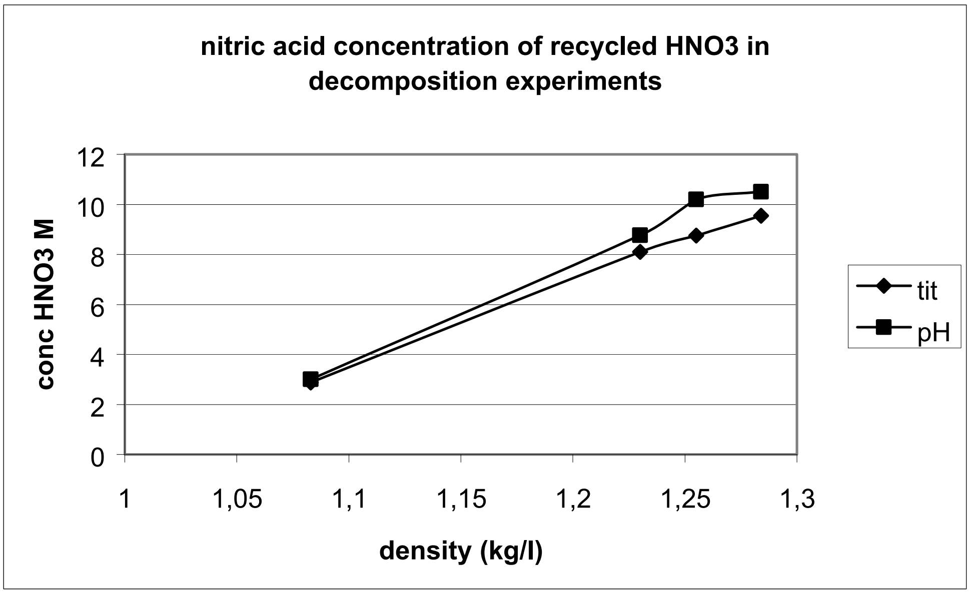

Figure 5.3: Density vs measured and determined pH

The liner from the smaller autoclave was weighed and its content described. Descriptions of sample 4 to 10 are given in table 5.3 and figure 5.4. The decomposition residue is very hygroscopic, the sample weight of residue Dest 11 had increased with almost 9% while left standing in the open air.

Figure 5.4: Residues from $Mg(NO_3)_2.6H_2O$ decomposition tests, top row from left to right: dest 4, 5, 6, bottom from left to right dest 7, 8, 9 and 10.

dest 4	purple red hard consistent lava like decomposition residue, hard to remove from liner
dest 5	surface purple red with thin white transparent layer, bulk contains cavities covered with white layer
dest 6	surface completely opaque white 'coaly flower' appearance, bulk contains cavities covered with white layer
dest 7	Bordeaux red and white, brittle
dest 8	grey, white and Bordeaux red, more brittle than 7
dest 9	grey, white and orange surface contains small cavities, like pumice
dest 10	like 9, a bit darker

Table 5.3: Description of magnesium nitrate decomposition residues

The residues were sent to the service lab of TNO Built Environment and Geosciences for analyses on bulk composition, LOI, nitrate and carbon. The results are given in table 5.4:

	MgO (%)	Fe_2O_3 (%)	NiO (%)	MnO (%)	Al_2O_3 (%)	H_20 (%)	LOI (%)	total (%)	NO_3 (%)	CO_2 (%)
DEST 2	61,52	8,79	0,47	0,13	0,11		31,81	102,83	23,08	n.a
DEST 3	48,35	1,51	0,17	0,03	0,02		47,23	97,30	39,83	n.a
DEST 4	21,41	2,81	0,14	0,04	0,06	-0,20	75,37	99,63	54,50	0,08
DEST 5	32,90	4,74	0,26	0,06	0,05	8,77	53,56	100,35	21,47	0,73
DEST 6	41,25	5,76	0,31	0,07	0,06	4,07	47,24	98,78	17,87	1,14
DEST 7	28,96	4,03	0,20	0,05	0,04	-0,25	65,73	98,78	42,94	0,43
DEST 8	35,34	0,92	0,11	0,02	0,01	-0,25	62,79	98,95	42,80	0,24
DEST 9	39,86	0,66	0,12	0,02	0,01	-0,28	56,49	96,88	43,02	0,04
DEST 10	34,58	0,65	0,10	0,02	0,01	-0,29	61,74	96,82	48,14	0,22
DEST 11	60,73	0,42	0,16	0,02	0,01	3,68	42,70	107,71	29,53	0,16

Table 5.4: Analytical results of the solid decomposition residue (TNO Built Environment and Geosciences)

5.5 Interpretation.

The main purpose of the decomposition experiments was to get an impression of the possibility to produce a magnesium hydroxide/oxide while at the same time reclaiming the nitric acid. Due to the limited number and the highly experimental character of these tests a lot of parameters were extensively varied which makes interpretation and correlation more difficult. One of the first parameters that will be looked at is the liner output/input ratio which, due to the loss of nitric acid, water and nitrogen oxides, is the simplest indicator for the reaction progress. This ratio is plotted in fig 5.5. The experiments have been divided into three groups: magnesium nitrate crystals, magnesium nitrate liquid and carbon dioxide atmosphere.

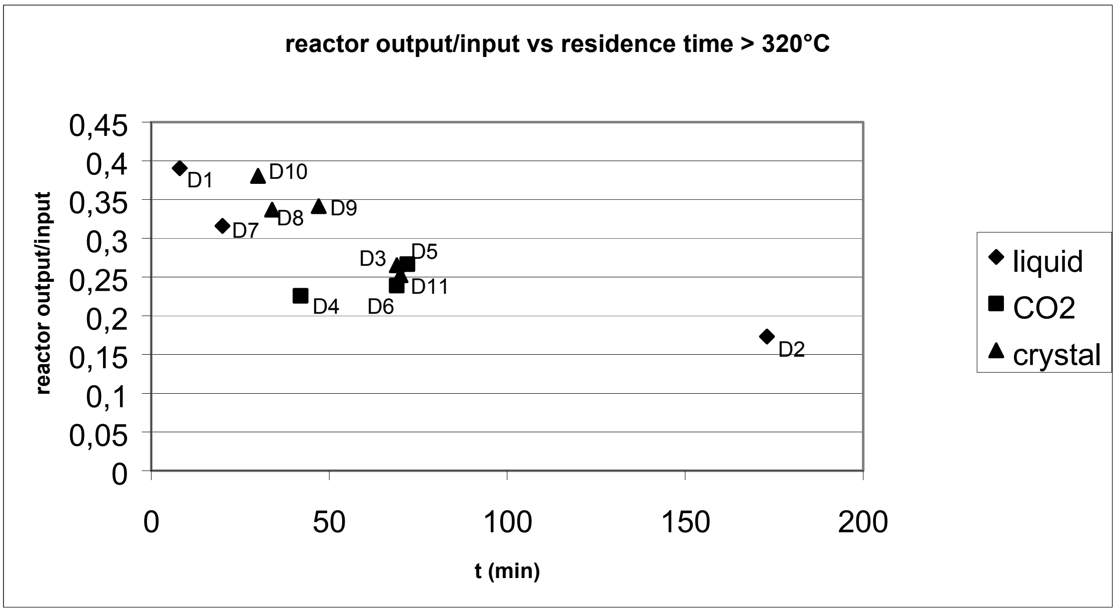

Fig 5.5: Output/input ratio of the decomposition experiments plotted against residence time above 320°C.

A decreasing trend is expected approaching a minimum which is determined by the metal oxide content of the samples, or, more in general, all remaining phases that are stable above 330-340°C. The calculated metal oxide content of the magnesium nitrate solutions is 11,0-12,5 %, for the crystals it is 13,0 to 15,0 %. Experiments Dest 3, 8, 9, 10 and 11 represent the most homogenous group of experiments and show a clear decreasing trend. Dest 1 and 7 plot below this trend because they have already lost a substantial amount of water during the heating stage and therefore their ratio will already be lower at the moment that a temperature of 320°C is reached. The ratio of Dest 2 gives an indication that the decomposition trend is not linear. Of the experiments carried out under carbon dioxide atmosphere Dest 4 plots well below the other experiments which is probably due to the sudden pressure drop caused by a leaking silver gasket.

Another parameter of importance is the removal of nitrate groups. This removal is presented as the nitrate content of the sample residue after decomposition divided by twice its Mg and Fe content. The removal is plotted against the residence time above

320°C in figure 5.6. This limit was chosen because most nitrate decomposition will occur above this temperature.

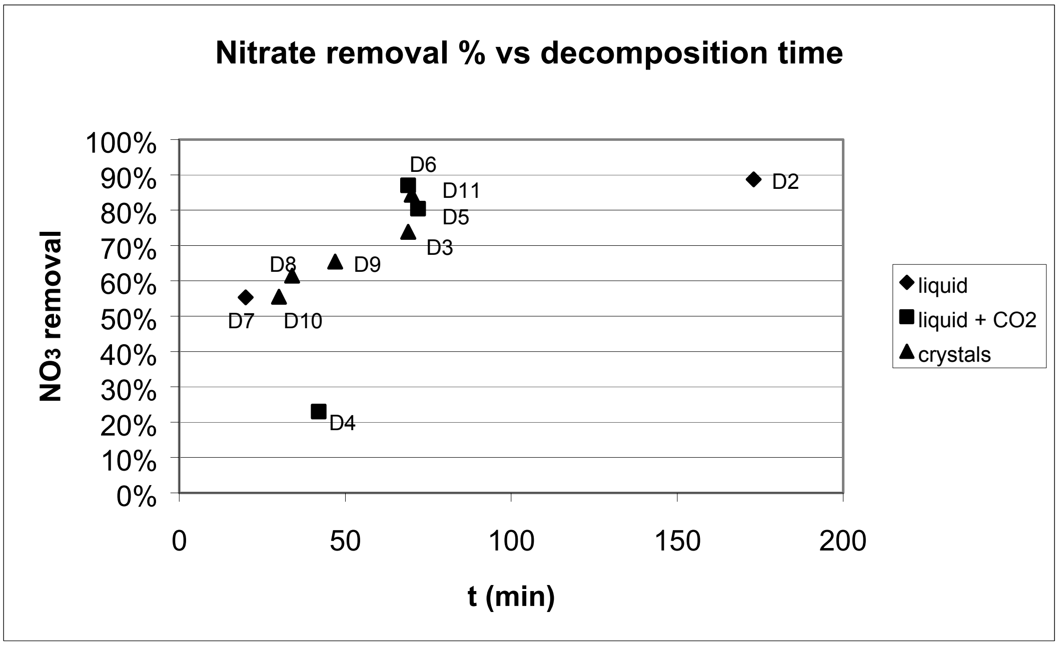

Fig 5.6: Relation between nitrate removal and residence time at decomposition temperature.

The magnesium nitrate decomposition experiments show a clear trend. The relatively high amount of nitrate still present in Dest 2 indicates that the decomposition process is probably non-linear. The calculated nitrate removal percentages are given in table 5.5. The low removal percentage displayed by Dest 4 is probably due to either the carbon dioxide pressure of 5 bar, the sudden pressure drop caused by the leaking silver gasket or the relatively low decomposition temperature or a combination of these.

	MgO %	Fe2O3 %	NO3 %	Mg mol	Fe mol	Mg+Fe mol	NO3 mol	Mg, Fe	NO3	removal %
	A	B	C	A'= A/40,3	B'= B/79,8	D=A'+B'	C'= C/62	D/D	C"= C'/D	(2-C")/2
DEST 2	61,5	8,79	23,1	1,54	0,11	1,65	0,37	1,00	0,23	89%
DEST 3	48,3	1,51	39,8	1,21	0,02	1,23	0,64	1,00	0,52	74%
DEST 4	21,4	2,81	54,5	0,54	0,04	0,57	0,88	1,00	1,54	23%
DEST 5	32,9	4,74	21,5	0,82	0,06	0,88	0,35	1,00	0,39	80%
DEST 6	41,3	5,76	17,9	1,03	0,07	1,10	0,29	1,00	0,26	87%
DEST 7	29,0	4,03	42,9	0,72	0,05	0,77	0,69	1,00	0,89	55%
DEST 8	35,3	0,92	42,8	0,88	0,01	0,90	0,69	1,00	0,77	61%
DEST 9	39,9	0,66	43,0	1,00	0,01	1,00	0,69	1,00	0,69	65%
DEST 10	34,6	0,65	48,1	0,86	0,01	0,87	0,78	1,00	0,89	56%
DEST 11	60,7	0,42	29,5	1,52	0,01	1,52	0,48	1,00	0,31	84%

Table 5.5: Removal percentage calculation

The nitrate removal percentages are calculated by dividing the MgO, Fe_2O_3 and NO_3 weight percentages by their molar weight and subsequently determining the NO_3/([Fe,Mg]) ratio. Originally every Mg, Fe ion is balanced by two nitrate ions, so the removal percentage is 2 - NO_3/([Fe,Mg])x100. The remaining hydroxide/oxide needed to balance Mg, Fe can be calculated by balancing the molar and weight percentages. This way, assuming that all the other metals have been decomposed to their respective oxides, a chemical composition formula for the residual magnesium phase can be calculated. The results of this calculations are given in table 5.5 and figure 5.6. Take notice that the H_2O content in the graph represents the actual water lost during LOI (= hydroxyl and hydration water), whereas the H_2O in the table represents the water remaining after subtracting the hydroxide groups needed to balance the magnesium ions (= only hydration water). The H_2O percentage in table 5.6 (water lost at <105°C) was left out of consideration since this water is very likely not to be part of a crystalline structure. All these calculations represent samples that due to their hygroscopic character have been re-hydrated to a certain extent!

	Mg	O	NO3	CO3	OH	H2O
DEST 2	1,00	0,45	0,24	0,00	0,86	0,00
DEST 3	1,00	0,15	0,54	0,00	1,16	0,00
DEST 4	1,00	0	1,65	0,00	0,34	2,74
DEST 5	1,00	0	0,42	0,02	1,54	1,56
DEST 6	1,00	0	0,28	0,03	1,67	0,82
DEST 7	1,00	0	0,96	0,01	1,01	1,65
DEST 8	1,00	0	0,79	0,01	1,20	1,00
DEST 9	1,00	0	0,70	0,00	1,30	0,42
DEST 10	1,00	0	0,91	0,01	1,08	0,73
DEST 11	1,00	0,22	0,32	0,00	1,24	0,00

Table 5.6: Calculated chemical fomula of the decomposition product.

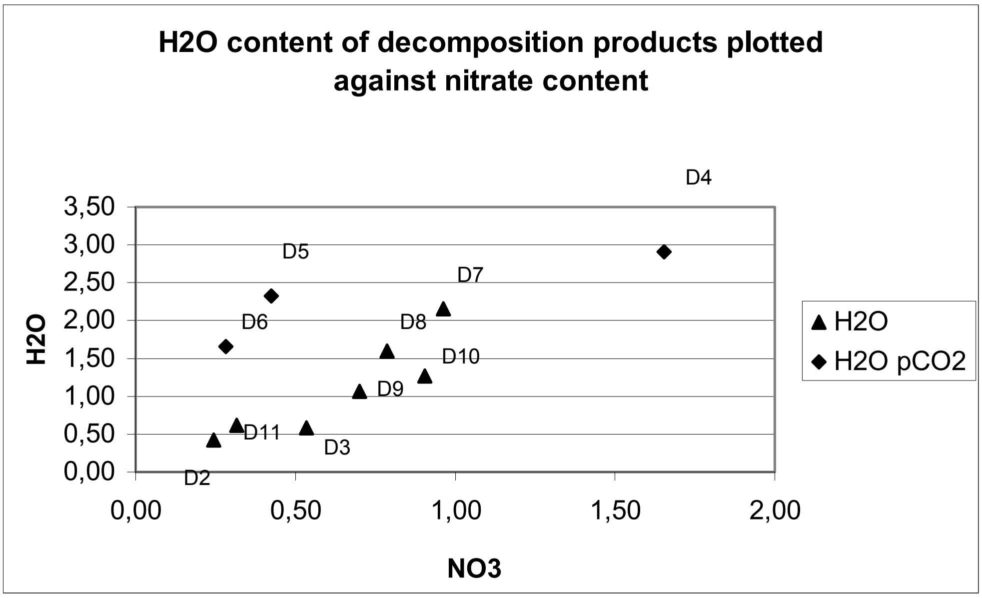

Fig 5.7: H_2O content of decomposition products plotted against nitrate content.

For the calculations it was assumed that all nitrates in the decomposition product were bound to magnesia since all the other metal nitrates decompose at lower temperatures. The seven samples from the experiments conducted in air show an almost linear correlation between nitrate and water.

Decomposition product Dest 4 seems to lie within this trend, probably because the carbon pressure in the end was lost. It is not unlikely, especially considering its low output/input ratio and the course of the decomposition temperature, which was relatively low, that Dest 4 had been transformed to an almost completely dehydrated or anhydrous magnesium nitrate which has been quickly re-hydrated. The formation of anhydrous metal nitrates under certain circumstances was also observed by Wendlandt (1958).

Sample Dest 5 and Dest 6 are deviating from the trend shown by the other decomposition products. Although their decomposition residence time and temperature are comparable to that of Dest 11 they contain more hydroxyl groups and hydration water. This indicates two possibilities:
1) the presence of carbon dioxide gas inhibits the breakdown of hydroxyl groups and hydration water but at the same time does not inhibit the decomposition of nitrate groups.
2) a decomposition product formed in the presence of carbon dioxide becomes more hygroscopic than a product formed under atmospheric circumstances.

Crystal fractionation coefficients.
The chemical analysis of the decomposition products shows that the products derived from the magnesium nitrate crystals are relatively low in iron, nickel manganese and aluminium. The ratios of these products represent the ratios of the original magnesium nitrate solution and the magnesium nitrate crystals. Based on the average ratios preliminary ratios have been calculated.

	solution	crystal	crystal/solution
Fe/Mg	0,1616	0,0269	0,1663
Ni/Mg	0,0096	0,0041	0,4290
Mn/Mg	0,0024	0,0007	0,3057
Al/Mg	0,0016	0,0004	0,2240

Table 5.7: Distribution coefficients of iron, nickel, manganese and aluminium with respect to magnesium in solution and incorporated in crystals

6 CARBON DIOXIDE SEQUESTRATION EXPERIMENTS USING MAGNESIUM NITRATE SOLUTIONS AND DECOMPOSITIONS RESIDUE FROM MAGNESIUM NITRATE.

6.1 Introduction

Several preliminary experiments were carried out to investigate the carbon dioxide sequestration possibilities and capacity of the residue the decomposition experiments:

- Low temperature (<250°C) distillation of HNO_3 under carbon dioxide atmosphere
- High temperature (>330°C) decomposition and simultaneous carbonatation of the magnesium(hydr)oxides formed.
- Aqueous precipitation of carbonates.

6.2 Low temperature (<250°C) distillation of magnesium nitrate solution under carbon dioxide atmosphere.

These experiments were conducted in order to investigate the stages of dehydration of magnesium nitrate solution in presence of carbon dioxide, the recovering of water and possibly some nitric acid. These relatively simple experiments were mainly conducted as a pre-study concerning the combined decomposition/carbonatation experiments.

The experimental set up was equal to the distillation/decomposition experiments as described in paragraph 5.2. Two hundred grams of magnesium nitrate solution from experiment 19 was put in a liner. The liner was placed in the smaller autoclave and heated. After each run the autoclaves were opened and its contents examined.

exp. no.	T_{set} (°C)	T_{max} (°C)	CO_2 (bar)	t (min)
seq 3	60	127	10	17
seq 4	75	102	5	742
seq 5	75/100	106	5	340
seq 6	120/150	151	5	222
seq 7	220	239	5	222

Table 6.1: Experimental data of the low temperature distillation of magnesium nitrate solution under carbon dioxide atmosphere.

6.2.1 Results

The temperature graphs are given in figure 6.1. The first experiment (seq 3) was conducted with a heating rate of 6°C per minute. Although the temperature controller was set at 60°C, the temperature rapidly reached a 127°C within 17 minutes. It was decided that this was too far from the originally planned experiment temperature and the experiment was ended. Experiment seq 4 was started with 5 bar and a heating rate of 3°C per minute. The temperature was set at 75°C. Despite the lower heating rate, the temperature once again increases rapidly above the desired value. This time the heating mantle was temporarily removed until the temperature did not increase anymore and the experiment was left for 10 hours at a temperature of 75°C.

For experiment seq 5 the temperature was initially set at 75°C. The temperature increased in the same way as seq 4 only this time the heater was not removed. The temperature peaked at 106°C after which the controller temperature was set at 100°C. It remained at this temperature for 5,5 hours.

The temperature for seq 6 was set at 120°C. During heating the temperature remained stable around 105°C for about 10 minutes. After this the temperature rapidly increased to 152°C during which the heating mantle was removed. The new temperature was set at 150°C and the experiment continued for 3,25 hours. After all above mentioned experiments the autoclaves were opened for examination though no transfer of gasses/fluids could be detected.

For the last temperature the temperature was set at 220°C. The temperature increased to 178°C were it stabilized for 10 minutes, after this the temperature rose again and started to oscillate for 1,5 hour between 180°C and 250°C. Finally it stabilized on 218°C were it remained for another hour.

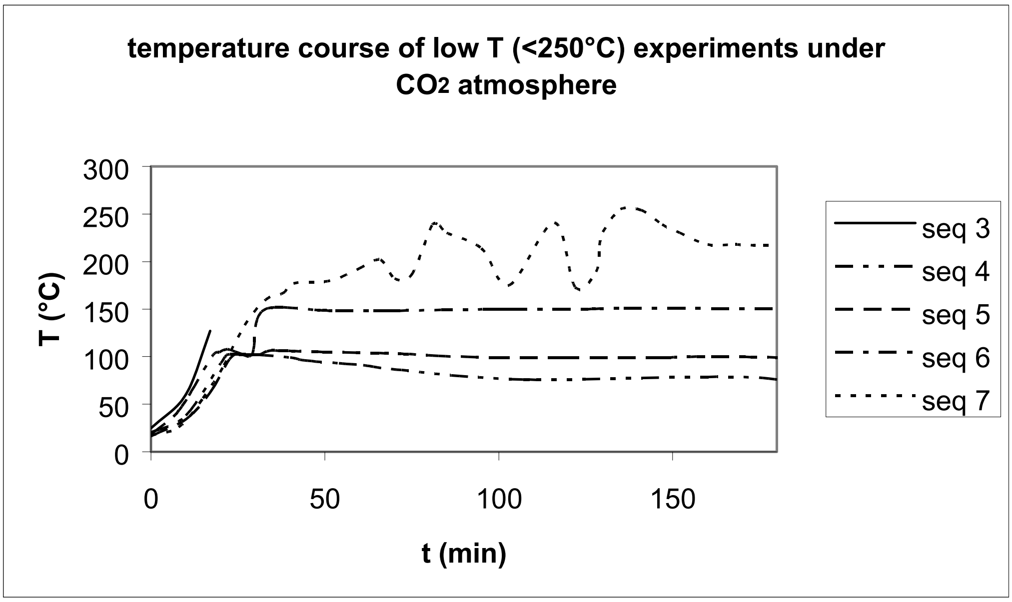

Figure 6.1: Heating curve of nitrate solution in 5 bar carbon dioxide.

After this experiment 50 ml (51,67 gr) of acidic fluid was collected in the liner of the larger autoclave. The smaller liner, still hot, contained a transparent paste which solidified grey/black upon cooling. The solidified magnesium nitrate was analysed on ICP and TGA, the results are presented in table 6.2 and figure 6.2.

	MgO	Fe2O3	NiO	MnO	Al2O3	LOI	Total
Seq 7	20,01	1,74	0,22	0,03	0,04	77,08	99,12

Table 6.2: Analytical data of the dehydrated paste from experiment seq 7.

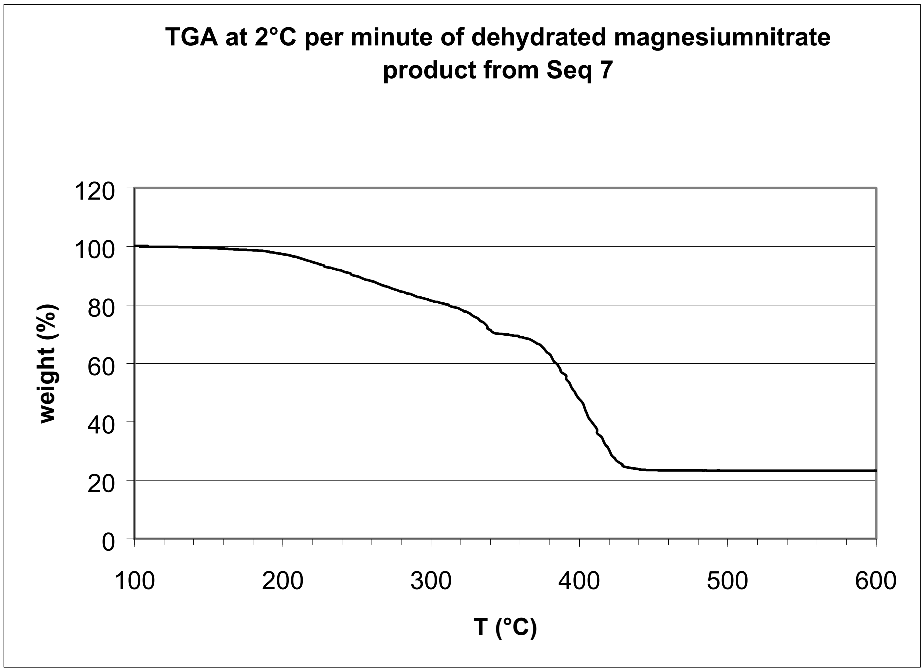

Figure 6.2: TGA of dehydrated magnesium nitrate sample seq 7

6.2.2 Interpretation.

These experiments were conducted in order to reveal whether the addition of carbon dioxide gas would have any unexpected and possibly uncontrollable side effect. Already the first experiment shows that in this set up temperature control is difficult. Also during other experiments the temperature would increase rapidly above the programmed temperature. This is possibly not a result of an exothermic reaction but an over reacting of the temperature controller. During heating of the magnesium nitrate three different endothermic processes occur: Melting, combined evaporation and dehydration of the magnesium nitrate hexahydrate and finally dehydration and nitrate decomposition of the magnesium nitrate dihydrate. All of these processes consume heat and make the heater work harder than for heating a normal aqueous solution. As soon as the endothermic processes are over, the bomb will be over heated which results in a sudden temperature increase.

It is found that below 150°C no significant water or nitric acid is evaporated or decomposed and apparently, compared to experiments Dest 2 and 3 boiling and decomposition temperature of hexahydrate shifts from ±120°C to ±180°C. This is in agreement with the fact that less water hydroxides were decomposed from the decomposition products from Dest 5 and 6 as already mentioned in paragraph 5.5.. If we recalculate the oxide analyses as given in table 6.2 to their respective low (20°) and high (220°C) temperature nitrates this we obtain the weight percentages as given in table 6.3.

	MgO	Fe2O3	NiO	MnO	Al2O3	N2O5	H20	Total
Seq 7	20,01	1,74	0,22	0,03	0,04	57,63	57,62	137,29
Seq 7	20,01	1,74	0,22	0,03	0,04	53,78	18,08	93,90

Table 6.3: Analytical results for the oxides from the residue from exp seq 7 recalculated to their respective nitrate and (hydr)oxide phases.

For the low temperature phases $Mg(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ $Mn(NO_3)_2.4H_2O$ and $Al(NO_3)_3.9H_2O$ were used for calculation. For the high temperature phases $Mg(NO_3)_2.2H_2O$, FeOOH, $Ni(NO_3)_2$, MnOOH and AlOOH were used. The high temperature calculations match best with the analytical results. Nevertheless it is not exactly clear what (meta)stable components may have formed at 220°C and 5 bar CO_2. According to Wieczorek-Ciurowa and Kozak (1999) al iron nitrate hydrate will have decomposed to FeOOH in air at 160°C. This is confirmed analyses from Gadalla and Yu (1990) who found that under varying circumstances (stagnant and flowing air, heating rates of 1°C/min and 10°C/min) all iron nitrate decomposed to FeOOH below 200°C. After the rapid breakdown of the basic nitrates the transition from FeOOH to Fe_2O_3 proceeds at a much lower rate.
For nickel at 220°C varying phases have been found depending on the atmosphere, in stagnant air basic nickel nitrate tetrahydrate $(Ni(NO_3)_2.2Ni(OH)_2.4H_2O$ has been found, whereas in flowing air anhydrous nickel nitrate ($Ni(NO_3)_2$) has been found. Although less relevant, $Ni(OH)_2$ was detected at 227°C in vacuum (Gadalla and Yu (1990). Aluminium nitrate nonhydrate decomposes at low temperatures and looses most of its water and nitrate groups below 170°C. Above this temperature a relatively slow dehydroxilation takes place.

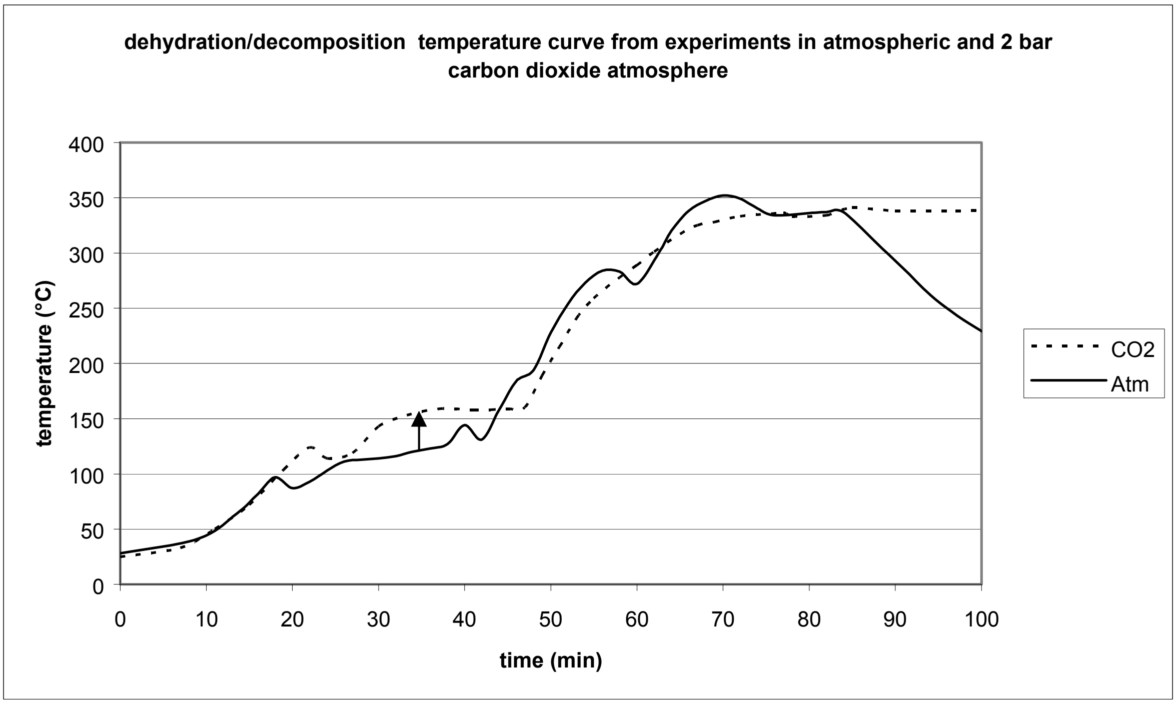

Fig 6.3: Temperature curve of atmospheric and carbon dioxide experiment. The arrow indicates the decomposition temperature shift.

It is obvious that the high temperature set of mineral phases gives the best fit to the analytical results for distillation residue seq 7. Regarding the calculated weight total of the residue at 220°C there is some 6% missing. The addition of 5 bar carbon dioxide in these experiments might be the reason that the assumptions made about the decompositions products are not valid. Figure 6.3 shows that the evaporation/decomposition temperature of the magnesium nitrate solution has been shifted by the addition of carbon dioxide. It is possible that the decomposition temperatures found in literature do not apply for this experiments and may have changed as well. Therefore it is possible that some decompositions were not as complete as assumed.

The TGA curve of the decomposition product at 220°C in figure 6.2 can be divided into two parts, first a relatively slow weight decrease of ±30 % that end s at 350°C, and subsequently a more rapid decrease of ±47 %. These weight percentages do not correspond to the calculated nitrate and water content of the decomposition product at 220°C and could indicate that in this decomposition trajectory an intermediate basic magnesium nitrate is formed.

There are no indications that CO2 is sequestered during the above described processes.

6.3 High temperature (>330°C) decomposition and simultaneous carbonatation of the magnesium(hydr)oxides formed.

One of the disadvantages of using magnesium hydroxide for dry carbon dioxide sequestration is that it has to de dehydroxylated at 350-375°C (Butt, Lackner et al 1996). In order to avoid an additional decomposition step it seemed useful to try and add carbon dioxide to the process of nitrate decomposition. The idea was to use the very moment of nitrate decomposition, when magnesium particles are probably highly reactive, for carbonate synthesis. Carbon dioxide was added to three of the decomposition experiments (dest 4,5 and 6) in order to see if simultaneous nitrate decomposition and carbonation is possible.

The set up for the simultaneous decomposition and sequestration experiments is, as described in paragraph 5.2, identical to the other decomposition experiments except for the fact that carbon dioxide was added.

experiment no	dec residue used	amount residue used	reaction media	CO_2 added (bar)	N added (bar)	T(°C)	t (min)	Appr. Reactor vol (ml)
dest 4	dest 4	44,8*	gas/solid	5	0	340	42	2500
dest 5	dest 5	26,9*	gas/solid	2,2	0	330	72	2500
dest 6	dest 6	24,0*	gas/solid	2	0	340	69	2500

Table 6.4: Experimental data of the high temperature sequestration experiments. * = residue from 200, 100 and 100 gr of magnesium nitrate solution, weighed after experiment.

6.3.1 Results

The analytical data are given in table 5.4. Photographs of the samples are given in figures 6.4a and 6.4b. The analyses of Dest 4 show no significant uptake of carbon dioxide. Despite the white appearance of samples 5 and 6 and white covered vacuoles only a small amount of carbon dioxide was captured by the decomposition residue. Remarkable is also the loosely bound water of Dest 5 and 6 that is lost below 105°C.

Fig 6.4a and 6.4b: Top view of liners with decomposition residue dest 5 and dest 6

6.3.2 Interpretation.

Some carbon dioxide, albeit a minor amount, has been incorporated in samples Dest 5 and 6. It indicates that there are possibilities, but further research is needed to explore the inhibiting mechanisms.

The first possible reason why carbon dioxide uptake is very little is a physical one. The decomposition experiments carried out were static and the only movements or channels being formed within the decomposition residue are caused by the decomposition itself. As can be seen in figure 6.4, the white layer which formed on top of the decomposition residue looks impermeable and slows down or even stops al transport of gases through the decomposition residue.

As already mentioned in paragraph 5.5, carbon dioxide influences the decomposition of magnesium nitrate. Removal of hydration water occurs at higher temperatures and therefore possibly inhibits the formation of magnesium oxide which can readily be converted to magnesium carbonate.

7 AQUEOUS PRECIPITATION OF MAGNESIUM CARBONATES.

7.1 Introduction

Compared to dry carbonation at higher temperatures, the aqueous route was chosen because it is fairly simple and offers the highest reaction rate. Disadvantage is that, unlike for dry carbonation at high temperatures, the reaction heat can probably not be used. Products likely to be formed under moderate aqueous circumstances are hydromagnesite ($(MgCO_3)_4Mg(OH)_2.4H_2O$) , dypingite ($(MgCO_3)_4Mg(OH)_2.5H_2O$) or nesquehonite ($MgCO_3.3H_2O$). Hydromagnesite is also known as 'light magnesium carbonate', dypingite is also known as 'heavy magnesium carbonate.' Theoretically spoken all of these magnesium carbonates are meta stable and will finally convert to magnesite. Nesquehonite is unstable and easily converts to more stable phases at relatively low temperatures. Hydromagnesite is very stable and spontaneous conversion to magnesite would require hundreds of years (Zhang et al. 2000). Light and heavy magnesium carbonates are the only economically interesting basic magnesium carbonates. They are applied as a inert vehicle and absorbent in pharmaceuticals, as a carrier of perfumes in cosmetics, as a reinforcing and smoke repressing agent in rubbers and as raw material for flame retarding and insulating products.

The preparation of hydromagnesite from various precursors under atmospheric circumstances was extensively studied by Botha and Strydom (2001). They have studied the influence of slurry pH, slurry temperature and both drying time and temperature upon the end product. They found that hydromagnesite was directly formed at temperatures above 55°C or that it could be made by drying low temperature synthesized magnesium carbonates at temperatures above 100°C. Slightly lowering the pH by addition of HCl improved the dissolution of $Mg(OH)_2$ and speeds up the reaction.

7.2 Experimental approach.

Two batches (dest 2 and 3) of the thermally decomposed magnesium nitrate were used for aqueous carbonation experiments. In total six aqueous magnesium carbonate precipitation experiments were carried out to investigate the carbonate forming ability of the magnesium nitrate decomposition products. Conditions of the experiments were chosen to be favourable for formation of hydromagnesite. Our experiments deviate from the experiments done by Botha and Strydom in this respect that they were carried out in an autoclave at higher pressure. For the experiments 5 grams of decomposition residue was weighed and mixed with 100 grams of water in a glass liner. After mixing the pH was measured. The liner was placed in a 600 ml autoclave. Two experiments were carried out at in carbon dioxide atmosphere at room temperature, two under carbon dioxide at 100°C and two under a mixed carbon dioxide/nitrogen atmosphere at room temperature. Gas/slurry contact was improved by stirring the sample vigorously at 600 rpm. The experiments ran, depending on the temperature and carbon dioxide concentration for at least one hour. The course of temperature and pressure was registered. After the experiment the liner was put in the oven at 90°C until all water had evaporated. Subsequently the liner containing the dried sample was weighed. Experimental parameters and data are given in table 7.1.

experiment no	dec residue used	amount residue used	reaction media	CO_2 added (bar)	N added (bar)	T(°C)	t (min)	Appr. Reactor vol (ml)
seq 8	dest 2	5,07	gas/slurry	10	0	25	105	500
seq 9	dest 2	5,00	gas/slurry	10	0	100	60	500
seq 10	dest 3	5,02	gas/slurry	10,5	0	25	145	500
seq 11	dest 3	5,00	gas/slurry	10,5	0	100	140	500
seq 12	dest 2	5,03	gas/slurry	1,2	4	25	170	2500
seq 13	dest 2	5,00	gas/slurry	1	9,4	25	140	2500

Table 7.1: Experimental data of the aqueous sequestration experiments.

7.3 Results

The course of pressure of four room temperature experiments is given in figure 7.1. Since the pressure in the other two experiments was heavily influenced by heating and cooling of the autoclave, the uptake of carbon dioxide was not clearly reflected and the pressure data were left out. Dry material input and output data are given in table 7.2.

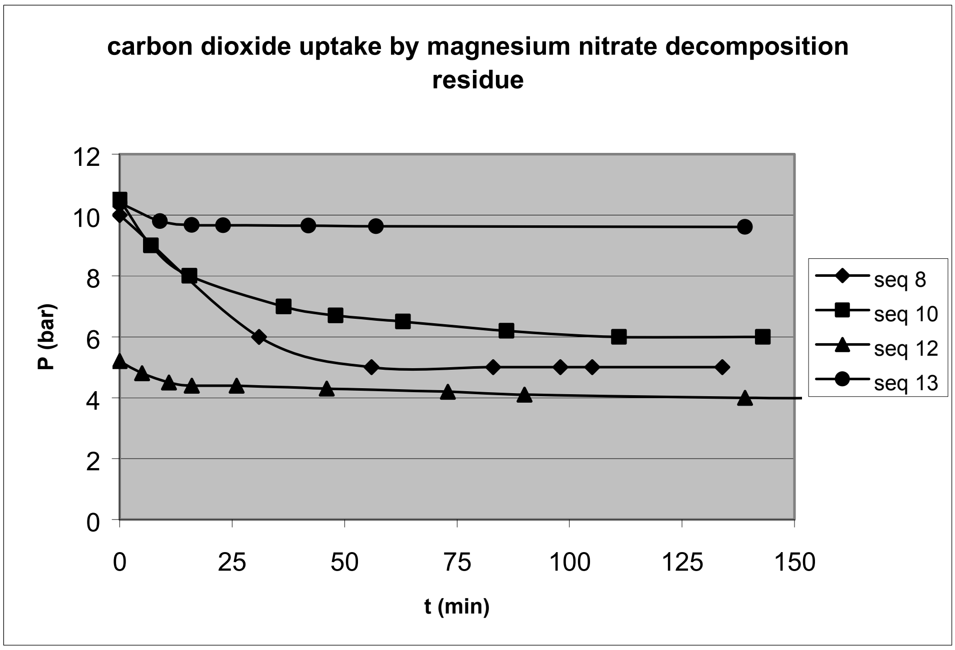

Fig 7.1: Carbon dioxide uptake by magnesium nitrate decomposition residue

sequestration experiment	seq 8	seq 9	seq 10	seq 11	seq 12	seq 13
material used	dest 2	dest 2	dest 3	dest 3	dest 2	dest 2
total dry in	5,07	5,00	5,02	5,00	5,03	5,00
Mg(OH)2 in	4,51	4,45	3,51	3,50	4,48	4,45
pH in	10,0	10,0	9,7	9,8	9,9	9,8
total out (90°C)	8,42	8,33	7,13	7,42	8,01	8,09
increase dm	3,35	3,33	2,11	2,42	2,98	3,09
dm out/in	1,66	1,67	1,42	1,48	1,59	1,62

Table 7.2: Input/output data of the sequestration experiments

All samples were sent to TNO for analyses of chemical bulk composition on ICP-MS, LOI, nitrate and carbon content. Data are given in table 7.3. Unfortunately the first attempt for carbon dioxide analysis failed and due to the small size of the samples too little of seq 8 and 9 was left for a second analysis.

	MgO (%)	Fe_2O_3 (%)	NiO (%)	MnO (%)	Al_2O_3 (%)	H_20 (%)	LOI (%)	total (%)	NO_3 (%)	CO_2 (%)
SEQ 8	34,41	4,70	0,23	0,06	0,07	6,81	56,30	102,59	10,70	n.a.
SEQ 9	34,30	4,63	0,24	0,06	0,05	6,46	55,65	101,38	10,33	n.a.
SEQ 10	33,33	0,87	0,10	0,02	0,01	4,51	61,17	100,01	24,47	18,12
SEQ 11	32,92	0,98	0,12	0,02	0,03	-0,20	63,94	97,81	20,88	20,83
SEQ12	37,78	5,86	0,30	0,07	0,07	3,06	58,42	105,56	n.a.	24,09
SEQ13	38,09	5,78	0,31	0,07	0,06	2,95	56,08	103,35	n.a.	24,81

Table 7.3: Chemical analyses and LOI of sequestered carbon dioxide

Two samples, seq 8 and seq 9, were analysed on XRD, the reflection patterns and corresponding mineral peaks are given in figures 7.2a and 7.2b.

7.4 Interpretation.

Graph 7.1 reveals a clear and rapid uptake of carbon dioxide by the basic magnesium slurry. It is shown by experiments 12 and 13 that exhaust gases can probably be treated without concentration step.

At first glance, the XRD patterns of both magnesium carbonates formed (seq 8 and 9) seem very much alike. The peak patterns do have a good match with the peak patterns from hydromagnesite and magnesium nitrate given in the powder X-ray diffraction (JCPDS) database. Seq 9 shows the sharpest peaks and the best peak/noise ratio and fits very well with the reflections of the hydromagnesite. Seq 8 displays considerably more noise and quite sharp peaks. A closer look at the graph reveals that some of the major peaks are slightly shifted towards lower angles and fit more closely to the magnesium nitrate reflection patterns.

Calculations were performed on seq 10 and 11, the only complete data set available. First of all the oxides were recalculated to their respective molar ratios and subsequently the molar ratios of all elements were divided by the magnesium molar ratio. After that the molar ratios were recalculated to their respective weight in oxides. In this way a simple estimation of the weight increase was obtained. The absolute change in molecular composition was calculated and is given in table 7.4.

	MgO %	NO_3 %	CO_2 %	H_2O % (calc)			
SEQ 10	33,33	24,47	18,12	23,09			
SEQ 11	32,92	20,88	20,83	22,03			
DEST 3	48,30	39,80	n.a	12,53			
Molar ratio calculated on 1 mol of Mg							
	Mg mol	NO_3 mol	CO_2 mol	H_2O mol			
SEQ 10	1	0,47	0,49	1,54			
SEQ 11	1	0,41	0,58	1,49			
DEST 3	1	0,54	0,00	0,58			
Weight ratio recalculated on 1 mol MgO							
	MgO (g)	N_2O_5 (g)	CO_2 (g)	H_2O (g)	total (g)	weight increase (%)	
SEQ 10	40,30	25,58	21,74	27,71	115,33	**45%**	*42%*
SEQ 11	40,30	22,10	25,32	26,77	114,48	**44%**	*48%*
DEST 3	40,30	28,92	0,00	10,45	79,67		
weight increase bold is calculated in italics is measured							
Partial weight increase split up per chemical compound							
		Δ N_2O_5 wt%	Δ CO_2 wt%	Δ H_2O wt%	Δ Total wt%		
SEQ 10		-4,19	27,29	21,67	44,8 %		
SEQ 11		-8,56	31,78	20,48	43,7 %		

Table 7.4: Calculated changes in chemical composition as a result from carbon dioxide uptake under pressure in an autoclave.

As can be seen, the bigger part of the weight increase is caused by the uptake of carbon dioxide. The other part of the weight increase is caused by the incorporation of crystal water in the hydromagnesite structure. Surprisingly, a substantial amount of nitrates have disappeared somewhere during the various stages of the experiments. Expressed in percentage of the original amount of nitrate present, the amount of nitrate removed varies between 12 and 24 %. Based on the molar ratios calculated we can derive a hypothetical mineral composition of the carbonate product formed. These compositions are given in table 7.5. Since the carbonate product was dried at 90°C, it was assumed that the magnesium nitrate hexahydrate was converted to a dihydrate and subsequently partially rehydrated.

	$4MgCO_3.Mg(OH)_2.4H_2O$	$Mg(NO_3)_2.3H_2O$	$Mg(OH)_2$
SEQ 10	80%	17%	3%
SEQ 11	85%	13%	1%

Table 7.5: Mineralogical composition based on chemical analyses and XRD data.

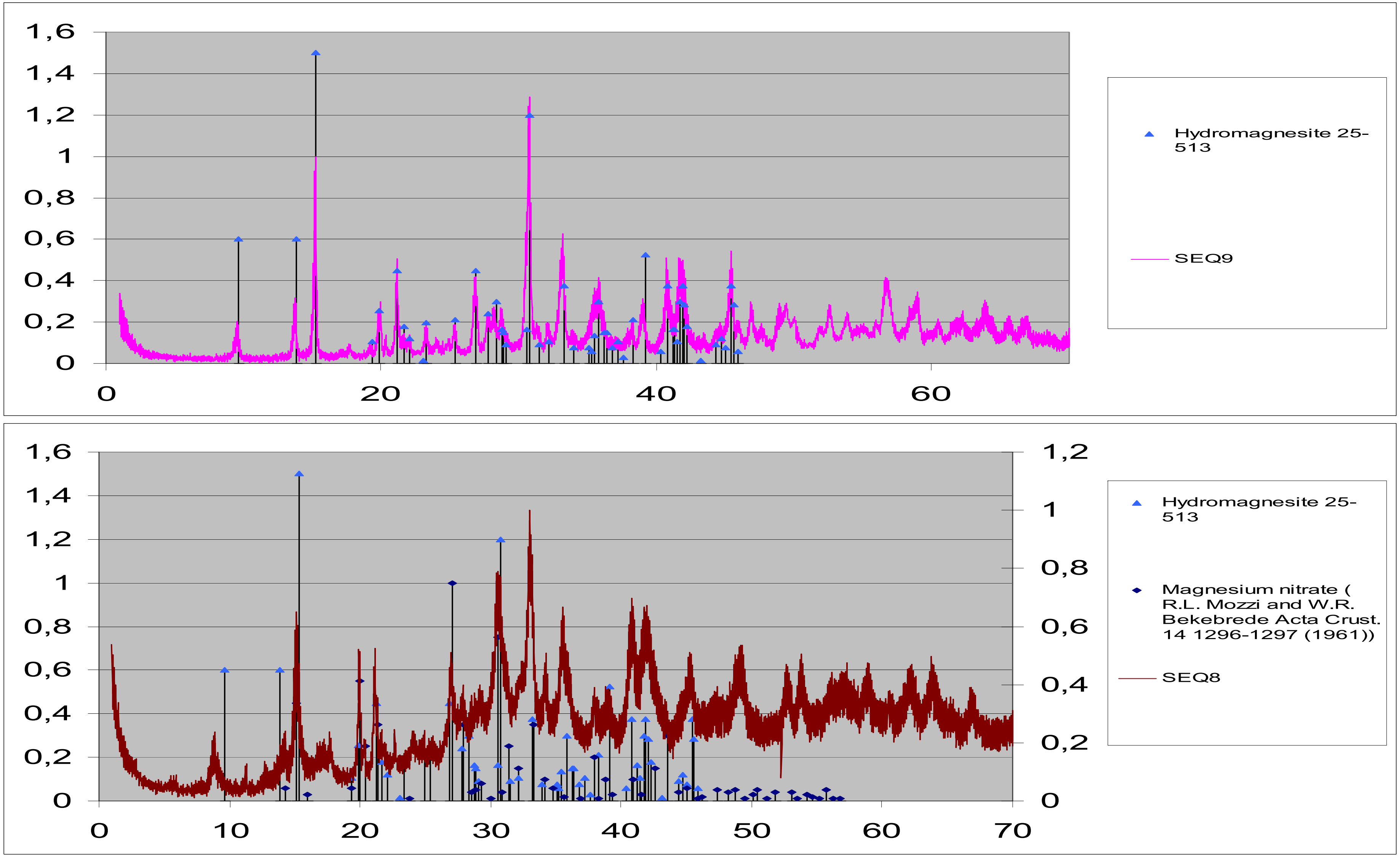

Fig 7.2a + b: XRD reflections of seq 8 and 9.

8 CONCLUSIONS.

Magnesium extraction from olivine using weak acids is not suitable for serious carbon dioxide sequestration. Acetic acid reacts too slow and is probably unstable at higher temperatures. The level of dissolved magnesium reached is non satisfactory. The pH reached during experiments is not high enough for direct carbonate precipitation.

Although dissolution of olivine in a potassium pyrosulphate solution yields reasonable results, the method is hampered by the relative low solubility of its products. Like the acetic acid experiments, the pH reached was not high enough to produce a magnesium solution suitable for instant carbon dioxide sequestration.

The experiments performed on the alkaline dissolution route with sodium sulphate offered no perspective. Although the walls of the autoclave liner were etched no olivine had gone into solution.

As expected, nitric acid proved to be very efficient for magnesium extraction from olivine. Olivine dissolution percentages of >80% were obtained in less than 4 hours at temperatures of 80°C. Very concentrated magnesium nitrate solutions can be obtained, at reaction temperatures of 90°C solutions of 84 gr/l Mg (which almost represents solid $Mg(NO_3)_2.6H_2O$) can be produced and given the right equipment these concentration can probably be higher.
The production of lower concentrated (± 60 gr/l Mg) solutions offers the possibility to separate the iron from the magnesium by crystal fractionation.

Comparable experiments using both commercially available olivine and anorthosite $(Na_{0.3}Ca_{0.7})(Al_{1.7}\ Si_{2.3})O_8$ revealed that the reaction rate of anorthosite is considerably lower than that of olivine. Added to the fact that anorthosite releases less ions suitable for carbon dioxide sequestration it can be concluded that anorthosite is not suitable for carbon dioxide sequestration.

At 350°C nitric acid can be recycled in one step magnesium nitrate hexahydrate decomposition. Magnesium nitrate hexahydrate decomposes by forming intermediate basic nitrate compounds, though decomposition products can be influenced by changing the atmospheric conditions. The decomposition process, as carried out in our research, is non linear.

Several ways of carbon dioxide sequestration were tested: Distillation of acidic magnesium nitrate solutions and simultaneous precipitation of magnesium carbonates. This was not successful. Decomposition of magnesium nitrates and simultaneous sequestration of carbon dioxide. Although the chemical analyses showed little carbon dioxide incorporation, the presence of a carbon dioxide phase was strongly suggested by the appearance of the decomposition product. Aqueous carbonation was performed on the decomposition product. Hydromagnesite was formed under relatively moderate circumstances. It was observed that to a certain extent the nitrate still present in the decomposition residue was replaced by carbonate.

9 RECOMMENDATIONS

Magnesium extraction by nitric acid seems, together with the HCl extraction route, to be one of the more effective means to produce a material suitable for carbon dioxide sequestration. Nevertheless, a considerable amount of energy is needed fro the decomposition of the nitrates. In this research it has been observed that carbon dioxide can, in certain circumstances, replace nitrate in a basic magnesium nitrate solution. It could be useful to further investigate and optimize this in order to obtain an economically sound way to perform mineral sequestration on carbon dioxide.

Due to the high cost of mining, transportation and processing, the surface mineralization of carbon dioxide will probably not be economically feasible. Certainly not at a very large scale. However, the research on this matter can be used for the development of carbon dioxide friendly methods for the production of magnesium products. With olivine replacing magnesite as a raw material for the production of refractories already 5 Mtpy of carbon can be saved, not to mention the reduction of the production energy needed.

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