APPLICABILITY OF POSSIBLE PRODUCTS FROM MINERAL SEQUESTRATION OF CO_2

APPLICABILITY OF POSSIBLE PRODUCTS FROM MINERAL SEQUESTRATION OF CO_2

A report prepared for:	Project Plan CATO: CO_2 capture, transport and storage
By:	Geochem Research BV Utrecht
Date:	April 15, 2005

The research in the CATO project is co-funded by a grant
from the Dutch Government in the framework of BSIK
(Besluit subsidies investeringen kennisinfrastructuur)

GEOCHEM RESEARCH BV, Maliestraat 21, 3581 SK Utrecht, Tel: 030 2219019, Fax: 030 2213066,
E-mail: research@geochem.nl, www.geochem.nl, KvK Utrecht: 33234308

CONTENTS:

SUMMARY

The present report deals with the applicability of potential products from mineral sequestration of carbondioxide.
Depending on the route of sequestration chosen, different reaction products will be formed. Direct sequestration will result in a carbonate, olivine, silica mixture, which is practically inseparable and will have little application possibilities. In a two step sequestration, strong acid magnesia extraction followed by magnesium hydroxide recovery and subsequent carbon dioxide sequestration, reaction products can easily be separated in different stages and washed. Sequestration with olivine will give the following products:

- Fine grained precipitated magnesite
- Precipitated silica
- Precipitated iron oxides
- A leached mineral residue

If anorthite is used the products potentially formed are:

- Fine grained precipitated calcium carbonate
- Precipitated silica
- Precipitated aluminium hydroxide
- A leached mineral residue

Magnesite
Magnesite ($MgCO_3$) itself is hardly used as an industrial mineral and usually serves as raw material for the production of caustic magnesia, dead burned magnesia or fused magnesia (all forms of MgO). These compounds are used for the production of refractories, and it is clear to see that the carbon dioxide has to be driven off again.
The magnesite purity needed for these products ranges from 90-95% $MgCO_3$.
Refractories account for ± 70% of the magnesite consumption. The non refractory market is determined by ceramics, agriculture, paper, rubbers, flame retardants and pharmaceuticals, in order of decreasing market volume and increasing purity demands.
Growth markets are water purification and the replacement of aluminium car parts by magnesia alloys. The total world market for magnesite is 10 to 12 million tonnes per year.
The magnesite precipitated from the sequestration process will very probably be polluted with metals and still contain some hydroxides. Therefore the application of this product must be sought in the low purity industrial grades and refractories. Although seemingly contradictive to the purpose of carbon dioxide sequestration, it is more profitable to use the extracted magnesium hydroxide directly for these purposes than to first sequester carbondioxide. One has to keep in mind that for every tonne olivine used a tonne of magnesite can be left unmined.

Silica
Silica is one of the most widespread used industrial minerals. The bigger part of it is consumed in the production of glass and ceramics. Most important in this area is the

purity (white colour) and consistency of the product quality. For coloured glass and container glass these requirements are less stringent.

Other applications of silica are foundry sand, silica brick, linings, hydraulic fracturing and in fluxes. In these applications the physical form, strength and crystallinity of the silica plays an important role. Precipitated silica does not meet these specifications and therefore is not suitable.

At first glance the market of fillers and extenders seems fit for fine grained precipitated silica. Nevertheless its high specific surface may cause problems.

Therefore, obvious applications seem to be in the field of microsilica and in the market for fillers and extenders. Possible applications are the replacement of sand in the production of fibreglass and ceramics and for metallurgical fluxes.

The total market for the silica product from sequestration is difficult to estimate and will be determined by its potential for replacement of other silica products. A rough estimate would be in the order of a few million tonnes per year.

Ironoxides

The iron oxides in from carbon dioxide sequestration can range from very fine $Fe(OH)_3$ to Fe_3O_4, depending on the precipitation circumstances. The precipitation of Fe_3O_4 is a very complex process and therefore less favourable.

By far the biggest application of iron oxide is as iron ore. The chemical demands are not very high, though fines are unacceptable. To make the precipitated iron oxides suitable for this application they have to be sintered first. The world market for iron ore in 2004 amounted to 1 250 million tonnes.

A few orders of magnitude smaller is the pigment market in which red, orange, yellow, brown and black iron oxides are sold. For this market the chemical demands are even less than for the steel market, provided that the colour is stable and long term reproducible. The grain size should be small. Other applications like catalysts and magnetic powder can be left out of consideration because their chemical requirements are too strict.

Aluminium oxides

If anorthite will be used for carbon dioxide sequestration, one of the products formed will be aluminium hydroxide. This can be used for the production of aluminium metal and minor quantities of abrasives and refractories. Some of the alumina can be used in the trihydrate form as a chemical. Specialty applications of ATH (aluminiumtrihydrate) include water treatment, and the production of flame retardants, zeolites and molecular sieves, catalysts and adsorbants, and aluminium fluoride.

It is possible that the aluminium hydroxide precipitated from carbon sequestration could serve as a raw material for the production of abrasives, refractories and aluminium metal. The total consumption of aluminium hydroxide in 2004 was 87 million tonnes.

Mineral residu.

From the original dunite fed to the process, 5 to 10 % will not react. Considering the good leaching characteristics of the residue, its application as fill in construction projects is an evident possibility. A more attractive use of the residue could be as a secondary ore of chromium.

Conclusion.

For all products potentially generated by mineral sequestration of carbon dioxide markets exist, ranging from high volume and low quality to low volume and high quality.

The small high quality markets require refining of the products, which would negatively influence their competitiveness. In addition, the high quality markets are too small to absorb any substantial amount of the products formed. The markets would be flooded and prices would collapse. Therefore, application of products should focus on the large volume, low quality markets. For those markets the precipitated products often have to be agglomerated.

If the mineral sequestration would be globally applied, even the large volume markets will suffer from the huge influx of raw material. Therefore, products from mineral sequestration of carbon dioxide can only be applied on a small scale and it is not likely that these products will decrease the cost of sequestration on a global scale.

1. INTRODUCTION

Mineral sequestration of carbon dioxide is a natural process associated with the weathering of certain rocks and minerals. The final stage of the process consists of precipitation of cations, mainly Ca^{2+} and Mg^{2+}, as relatively insoluble carbonates. The overall process is slow but exothermic.

The main goal of artificial CO_2-sequestration is to improve the kinetics of the natural process without loosing its energy advantage. Another important aspect is the potential value of the products from mineral sequestration, such as silica and magnesium carbonate.

In an earlier report an inventory of a large number of silicate minerals including their reactivity and availability has been established (Geochem Research 2005). The most suitable minerals for sequestration appear to be the Mg-silicate olivine, and the Ca-silicates anorthite and wollastonite. Both olivine and anorthite occur in large masses. Wollastonite is relatively rare and therefore expensive. Important products generated from these minerals are silica and magnesite.

From the amount of mineral involved it becomes clear that artificial sequestration, if feasible, will have to play a modest role in carbon dioxide fixation. Nevertheless, the value of the products makes it worthwhile to consider the process for limited application. For example the price of precipitated silica varies from 10 to 65 €/tonne and raw magnesite is in the order of 50 €/tonne. On the other hand olivine rock costs only 15-20 €/tonne CIF Rotterdam.

The purpose of this report is twofold: to give an impression of the quality of the sequestration products required for various applications and to support an economic evaluation of the mineral sequestration process. Possible applications of the sequestration products have been investigated and are described.

For each product the following topics are dealt with:
- general description of the product
- uses and qualities
- potential use of the sequestration product
- prices

In addition to the amount of mineral needed, the market size of the products generated by sequestration is an important factor in the feasibility of the method. Products that cannot be usefully applied will have to be disposed off. It should be realised that considerable space is needed for such deposition. For example, when using olivine, the amount of solid material roughly increases by a factor 2 in weight and a factor 4 in volume during the process.

2. POTENTIAL PRODUCTS FROM CO_2 SEQUESTRATION

2.1 The sequestration process

There are many ways to perform the carbon dioxide sequestration reaction. First of all there is the choice of silicates (olivine, wollastonite, anorthite) to be used for reaction, and second, the reaction can be done in two different ways: by direct sequestration or a two-stage process. The products formed after the reaction will strongly depend on the choices made.

The overall reaction between a silicate mineral and acid will roughly proceed according the next equation:

$$1)\ (Mg^{2+}, Fe^{2+}, Ca^{2+}, Al^{3+})_x\,(Al^{3+}, Fe^{3+}, Si^{4+})_y\,O_z + wH^+ + vAnion^- \rightarrow$$
$$aMg^{2+} + bFe^{2+} + bCa^{2+} + dAl^{3+} + eSiO_2(s) + fH_2O + vAnion^-.$$

Basically, the silicate and acid are transformed to precipitated silica and a salt solution. If weak acids, like carbon dioxide, are used the reaction will proceed very slowly and there is a considerable chance that other solids (e.g. $CaCO_3$ and $MgCO_3$) will precipitate as well. Also, it is questionable if the silicate mineral will go completely into solution. If the carbon dioxide reaction will proceed according to the above equation, the silica and carbonate will form a fine-grained mixed precipitate.

In order to avoid this, multi-step processes can be used in which a strong acid, such as hydrochloric or nitric acid, is used to dissolve the silicate mineral. These methods will be called pre-treatment methods. The dissolution agent can be re-generated from the solution after sequestration of the carbon dioxide by carbonate precipitation and recovery of other useful products. The process would evolve as follows:

- dissolution of the silicate in a strong acid
- separation of the silica
- precipitation of the carbonate
- separation of the carbonate
- precipitation of other products from the salt solution
- regeneration of the acid.

It is also conceivable that the dissolution agent is not regenerated but neutralised in order to form a useful product.

2.2 Products generated

Depending on the mineral and the type of process used, a number of solid materials remain after the sequestration process is completed.
In this report two mineral options are considered:
1) sequestration using olivine
2) sequestration using anorthite

Wollastonite is considered to expensive for CO_2 -sequestration purposes.
In principle, sequestration with pre-treatment will generate the same products as direct sequestration.
In case olivine, a high quality dunite or serpentine is used as a sequestration mineral, four substances will remain:

- Silica
- Magnesite
- Iron oxides
- Non reactive mineral residue

The silica is precipitated as a gel. Depending on the process route chosen, silica and magnesite are mixed or separated from each other. In case of direct aqueous carbonation it is impossible to separate the two products formed. For this mixture probably bulk applications have to be found. If the magnesium or calcium is extracted from the minerals and the silica removed prior to carbonation, more specialized applications can be considered. Depending on the pH and the redox potential of the reaction, Fe will remain in solution during silica precipitation. After removal of the silica it can be precipitated as iron(III)(hydr)oxide or as magnetite (Fe_3O_4).
If an impure dunite or peridotite is used the olivine mineral may contain a certain amount of calcium. This will be precipitated with the magnesite and form an impure magnesite or dolomite.
The use of anorthite as a sequestration mineral will result in the production of calcite and aluminium hydroxide. Table 1 summarises the amounts of various minerals and products involved. In all cases it is assumed that the reactions take place in aqueous environment.

1 t CO2 + 1.59 t olivine + 0.41 t water → 1.91 t magnesite + 1.09 t silica
1 t CO2 + 2.09 t serpentine + 0.27 t water → 1.91 t magnesite + 1.45 t silica
1 t CO2+ 6.32 t anorthite + 2.86 t water → 2.27 t calcite + 3.55 t Al-hydroxide + 4.37 t silica

Table 1: Amounts and types of product generated in various sequestration reactions

These amounts are valid for pure minerals. In case dunite is used about 0.1 tonne of iron oxides will be produced replacing roughly an equal amount of magnesite.
It should be emphasized here that the production of aluminium hydroxide and calcite from anorthite is largely hypothetical. The precipitation process as well as the speciation of the formed products needs investigation.

3. MAGNESIUM CARBONATE (MAGNESITE)

3.1 Introduction

In the next section the industrial magnesium minerals and their applications are considered. Magnesium metal and the magnesia compounds that can be produced directly or indirectly from the precipitated magnesium carbonate from CO_2 sequestration will be included in the survey.
In most cases the sequestered CO_2 has to be released again in order to make magnesium metal or magnesia compounds. Although this seems counter-productive, one has to realise that for all carbon dioxide released from the precipitated magnesium carbonate, natural magnesium carbonate or magnesite can be left unmined. Therefore, the production of these compounds contributes to the reduction of greenhouse gas albeit in an indirect way.

3.2 Uses and qualities

3.2.1 Magnesium in minerals and natural solutions.

Magnesite belongs to the class of carbonate minerals. It is typically white or colourless when pure, and displays shades of grey, yellow, brown or black when impurities, like iron, are present. There are two types of magnesite: crypto-crystalline or amorphous magnesite and crystalline or macro-crystalline (sparry) magnesite depending on the genetic process.

Magnesite is characterized by:

- a density between 2.9 and 3
- a hardness of 3,5 to 5

Magnesite is the principal source of magnesium compounds. Magnesium is the eighth most abundant element in the earth's crust and can be found in 60 different minerals. The most important in terms of commercial value are:

- Magnesium carbonates (magnesite and dolomite)
- Magnesium hydroxide (brucite)
- Magnesium silicates (olivine and serpentine)

Magnesium is also present as salts (chlorides and sulfates in brines and as cations in seawater. The latter contains an average of 4,17 $MgCl_2$ or 2,1 g/l MgO. It should be noted that brucite ($Mg(OH)_2$), is a hydroxide of magnesium that occurs as large tabular crystals and as fibrous or lamellar masses. It is typically white, but may appear light grey, blue or green.

Magnesite contains a maximum of 47.8% MgO. Iron can substitute for magnesium to form minerals with intermediate compositions between magnesite ($MgCO_3$) and siderite ($FeCO_3$).

3.2.2 Magnesia compounds

Magnesite is a widely mined and consumed industrial mineral. In the industry the mineral name magnesite is generally used mistakenly for various products derived from natural magnesite, brines or seawater. Most magnesite is not used in its carbonate form. For example, the bigger part of the world consumption is as raw material for the production of dead burned magnesia, often referred to as magnesite, a refractory material for metallurgical purposes. A short explanation of magnesia products and their production follows:

Magnesite

The present world production of magnesite from natural resources is 10 to 12 Mt/yr. Of the total world production 9.800 Mt is produced from mined magnesite and 1.500 Mt is from seawater or brines. Mined magnesite is produced in the form of $MgCO_3$. Magnesite from brines is precipitated as an hydrated carbonate/hydroxide complex $(MgCO_3)_3.Mg(OH)_2.xH_2O$.
Pure magnesite is composed of 47,8% MgO and 52,2% CO2. Mined magnesite generally contains a few percent of impurities like SiO2, CaO, Fe_2O_3 and Al_2O_3. Silica and calcium oxide contents may be in the order of a few percent, iron and aluminium oxides in the order of a few tenths of one percent. This means that ore grade magnesite contains about 95% of pure magnesite. Lower grades are used for agricultural purposes. Magnesite contents may be as low as 90%. On the other hand, chemical applications need magnesite grades of more than 99.5%.

Precipitated magnesite

Precipitated magnesite is usually prepared from brines by adding a soluble carbonate. The chemical is essentially used in two forms: light and heavy, the difference being the number of water molecules that are included in the compound. Light magnesium carbonate has the empirical formula $(MgCO_3)_3.Mg(OH)_2.3H_2O$, and heavy magnesium carbonate has the formula $(MgCO_3)_3.Mg(OH)_2.4H_2O$. Magnesium carbonate can also be produced by saturation of dolomite with aqueous carbon dioxide under pressure. Increasing the temperature precipitates the calcium carbonate. After filtration, the solution is heated to near boiling, so that water and any remaining CO_2 are vaporised, and magnesium carbonate precipitates, usually as light magnesium carbonate.

Caustic calcined magnesia

Magnesite, from both natural sources (primarily magnesite) and synthetic sources (seawater, natural brines or deep sea salt beds), is converted into caustic calcined magnesia by calcining to between 700°C and 1000°C, driving off 96-98 per cent of the contained carbon dioxide. Caustic calcined magnesia is both an end product and an intermediary step in the chain of magnesia products.

Deadburned magnesia

Further calcining of magnesite at higher temperatures between 1750-2200°C results in the largely inert product, deadburned magnesia. Heating to this level drives off all but a small fraction of the remaining carbon dioxide to produce a hard crystalline non-reactive form of magnesium oxide known as periclase. Deadburned magnesia exhibits exceptional dimensional stability and strength at high temperatures.

Fused magnesia

Fused magnesia is produced in a three-phase electric arc furnace. Using high grade magnesite or calcined magnesia as raw materials, a period of 12 hours is required for the fusion process at temperatures in excess of 2750°C. The process promotes the growth of very large crystals of periclase (>1000 microns compared with 50-100 microns for dead burned magnesia) with a density approaching the theoretical maximum of $3.58 g/cm^3$.
Raw magnesite used for the production of dead burned or fused magnesia should at least contain 95 wt% $MgCO_3$.
There are two grades of fused magnesia:

- Refractory Grade Fused Magnesia, used for the manufacturing high temperature bricks
- Electrical Grade Fused Magnesia, used as electrical insulating material in ceramic sheaths for heating elements

3.2.3 Industrial applications for magnesia compounds

Refractories

By far the biggest market for magnesia compounds is the refractory market. Nevertheless, consolidation within the refractory industries, technologic development in the steel making industry and the production of higher quality refractory materials lead to a decrease in consumption of magnesia compounds. At this moment China is the biggest supplier with low priced dead burned magnesia in the low- to medium grade markets. Although small compared to the refractory market, the environmental market accounts for the biggest consumption of caustic calcined magnesia.

Steel	70%
Cement and lime	7%
Ceramics	6%
Glass	4%
Chemicals	4%
Non-ferrous	3%
Others	6%

Table 2: Consumption of magnesia refractories in the industry

Non-refractory applications

As a general rule the large volume non-refractory markets use the lower quality magnesia and low volume markets use high quality magnesia. The world markets for chemical magnesia can be classified into four major categories, based on application:

- Agriculture
- Low purity industrial grade
- High purity industrial grade
- Super high purity grade

Agriculture

This market is dominated by low quality (80-90% MgO) natural magnesia where the volumes involved are high and the prices are low. Magnesia is used in animal feeds as a magnesia supplement to prevent hypomagnesaemia, and also as an additive for soil applied fertilizers.

Low purity industrial grade

The major industries consuming low purity magnesia are construction, paper pulp, magnesium chemicals and niche agricultural markets. Magnesium oxide with a carefully controlled reactivity is used in special cements for the production of light weight insulating boards and fire doors for the construction industry. These cements are also used for industrial flooring and for rapid high strength repair to motor ways and airport runways.

Magnesia is used in both the bleaching and the pulping processes in the production of paper. It is a whitener and improves the consistency of paper. More often calcium carbonate (ground calcium carbonate and precipitated calcium carbonate) is used. Further it is used as a combustion regulator in cigarette paper

Natural magnesia is usually used in the pulping process where chemical and physical properties are less important. In oxygen bleaching the fine controlled particle size and reactivity of synthetic magnesia helps protect the cellulose fibres during the bleaching process.

High purity industrial grade

This sector requires medium quality grades of magnesia and synthetic products dominate the market. It is the controlled chemical and physical properties of the magnesia, in particular it's reactivity, which determines its use in these applications.

Industrial Applications vary from anti-scorch protection in polychloropropene rubbers, friction linings in brake shoes and clutches (stabilizer in automotive PVC and reinforcing agent in plastics and rubber), viscosity modifiers in glass to pH control in leather tanning.

Super high purity grade

These markets are for chemical magnesia products of the highest quality. They are characterized by being small volume high value sectors. Supply is limited to those companies with the ability to produce >99% MgO and $Mg(OH)_2$ products. The market segments are pharmaceuticals, rubbers and polymer additives, detergent manufacture, flame retardants, transformer steel coatings, lubricating oil additives and high purity chemicals.

Magnesite has pharmaceutical applications as antacid (usually in the form of $Mg(OH_2)$) for the neutralisation of digestive acid. When in the form of $MgCO_3$, it is usually precipitated from either a solution derived from the dissolution of dolomite ($CaMg(CO_3)_2$) ('light' magnesium carbonate) or from a mixture of hot magnesium chloride and sodium carbonate ('heavy' magnesium carbonate). Magnesium carbonate as a diluter can be found in concentrations up to 45% wt in some tablet formulations. In addition, its absorptive properties also lead to its use as a flavour absorber in tabletting processes. It is used as a mild abrasive in toothpaste and as anti caking and flowing agent in talc powder.

Production of magnesium

Throughout the world, magnesium is currently manufactured by two methods, electrolytic reduction of magnesium chloride or thermal reduction of dolomite. Electrolytic recovery of magnesium requires a magnesium chloride feedstock that is normally prepared from seawater or brines. Electrolytic cells are used to recover magnesium from either hydrous or anhydrous magnesium chloride. Essentially, magnesium chloride fed to an electrolytic cell is broken down into magnesium metal and chlorine gas by direct current at 700°C. Graphite electrodes suspended in the bath serve as anodes, and steel rods serve as cathodes. After the current breaks down the magnesium chloride into chlorine gas and molten magnesium, the metal formed at the cathode rises to the surface of the bath where it is guided into storage wells. Chlorine and hydrogen chloride gases generated at the anodes are collected and pumped to a hydrochloric acid plant for recycling.

There are two ways of thermal production of magnesium metal: the Pidgeon process, using an external heat source, and the Magnetherm process, using heat generated by the electrical resistance of the reactants. In the Pidgeon process, dolomite and ferrosilicon are formed into briquettes and heated in a retort under vacuum. Magnesium oxide in the dolomite reacts with the ferrosilicon to produce magnesium vapour, which is cooled and condensed in a separate section of the retort.

In the Magnetherm process, calcined dolomite, ferrosilicon and alumina are heated under vacuum. Alumina reduces the melting point of the slag produced by the dolomite ferrosilicon reaction to make resistance heating practical. Magnesium vapour is cooled and condensed in a condensing chamber.

Country	Capacity (tpa)
Brazil	12.000
Canada	127.000
China	133.600
France	17.000
India	900
Israel	27.500
Kazakhstan	50.000
Norway	35.000
Russia	75.000
Serbia/Montenegro	5.000
Ukraine	60.000
United States	83.000
Total	626.000

Table 3: Production capacity of primary magnesium metal yearend 2000.

In 18 of the plants the raw material used is dolomite($CaMg(CO_3)_2$), in six plants carnallite ($KMgCl_3.6H_2O$) is used, in three of them magnesite, in two plants brines, and in one asbestos is used. The magnesium from brines, carnallite and magnesite is produced by electrolytic processing, the other two magnesium sources use thermal reduction.
Because of the high projected growth rate in magnesium consumption, new plants will be in production shortly in the following countries: Australia, Congo, Canada, Iceland, The Netherlands and The United Arab Emirates. Although the world demand for magnesium is growing, it is not growing fast enough to support the additional production of all the new plants in this countries.

Other applications.
Magnesium compounds are further used in the following products and applications: soap, paint, ceramics, production of ink, cacao winning and welding fluxes.

3.3 Production, markets and prices

3.3.1 World production of mined magnesite

Current world production of magnesite is 10 to 12 Mt/yr, which represents a slight increase over previous years. Almost half of the total production is from Asia, especially China and Korea (South and North). In 2002, China maintained it's position as the world's primary producer with 3.700.000 metric tons. Turkey occupies second place with 2.000.000 tons, followed by North Korea and Russia. Of the total world production 9.800 Mt is produced from mined magnesite and 1.500 Mt is from seawater or brines. The most important of the magnesia compounds is dead burned magnesia accounting for 9.700 Mt, followed by 1.700 Mt for caustic calcined magnesia.
Resources from which magnesium compounds can be recovered range from large to virtually unlimited and are globally widespread. Identified world resources of magnesite total 12 billion tons, and of brucite, several million tons. Resources of dolomite ($CaMg(CO_3)_2$), forsterite (Mg_2SiO_4), and magnesium-bearing evaporite minerals are enormous, and magnesia bearing brines are estimated to constitute a resource in the order of billions of tons. Magnesium hydroxide can be recovered from seawater.

	Country	**1990**	**1999**	**2000**	**2001**	**2002**
1	China[e]	2,170,000	2,450,000	4,070,000 [r]	3,580,000 [r]	3,700,000
2	Turkey	845,000	1,724,700	2,672,100	2,000,000 [e]	2,000,000
3	North Korea	1,600,000	1,000,000	1,000,000	1,000,000	1,000,000
4	Russia[e]	1,600,000*	900,000	1,000,000	1,000,000	1,000,000
5	Austria	1,179,000	749,000	726,000	700,000 [e]	700,000
6	Slovakia	877,840**	918,000	1,000,000 [r]	447,000 [r]	500,000
7	Greece [e]	650,000	495,100	500,000	500,000	500,000
8	Australia	360,115	280,500	349,800	605,300 [r]	484,500
9	India	355,033	360,100	365,080	370,000 [e]	380,000
10	Brazil	308,300	259,800	279,900	265,750 [r]	270,000
12	Canada [e]	180,000	180,000	180,000	180,000	180,000 [p]
	Others	490,524	846,800	949,120	898,950	882,500
	Total	11,420,000	10,164,000 r	13,092,000 r	11,547,000 r	11,597,000

Production data in metric tonnes
e = estimate * = USSR
r = revised ** = Czecho-Slovakia
p = preliminary (Sources: USGS Minerals Yearbook, Les Conseillers NGI (internal study))

Table 4: Development of world magnesite production from 1990 to 2002

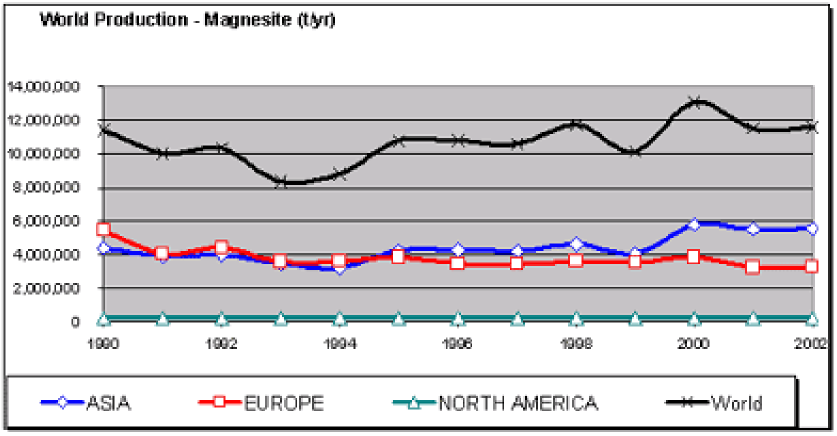

Figure 1: Development of the world production of magnesite from 1990 to 2002

3.3.2 Markets for magnesium compounds

Magnesium production

A considerable part of the world's mined dolomite and magnesite is used for the production of magnesium metal. Although, over the last few years, the total world production of magnesia has considerably increased, due to the growing replacement of aluminium car parts by magnesium alloys, the overall production in the western world has decreased. This is caused by the closure of plants in Europe and the shift of production to Russia and China.

Magnesium metal is 33% lighter than aluminium. According to data reported to the IMA (International Magnesium Association), aluminium alloying remained the largest end use for magnesia in the world, with almost 40% of the shipments. Die-casting, with 35% of the total, was second, followed by iron and steel de-sulphurisation with 16%. The primary world production in 2002 was 429,000 metric tonnes. Next to that a considerable part from the magnesium is recovered by recycling (for the US alone already >70.000 tpa).

Growth Markets

<u>Water purification</u>

Water treatment applications for magnesia continue to grow. Some companies have shifted from traditional neutralization reagents such as caustic soda and lime to magnesium hydroxide. Magnesium hydroxide, although more costly than the traditional reagents has several advantages including reduced sludge generation, removal of more dissolved heavy metals from the waste water stream, and magnesium hydroxide's buffering capacity. Magnesium hydroxide is safe and easy to handle. It buffers around pH=9,5 allowing a more controllable neutralisation reaction and reduces the risk of high pH discharge. This way re-dissolution of precipitated metal hydroxides is prevented.

Another important environmental application for magnesia is stack gas scrubbing. Combustion gases are filtered through an magnesium hydroxide suspension in which sulphur dioxide is retained to form an magnesium sulphate solution.

Flame retardants

Magnesium hydroxide has some advantages over the commonly used flame retardants. Compared to halogen based flame retardants, it does not release poisonous gases upon combustion. Its refractory nature leads to char formation during a fire, reducing smoke emission.

Other

Some high purity magnesite is used for the production of glass. Lightly calcined magnesite (LCM) containing 2-10% CO_2, called caustic magnesite is used for a wide variety of industrial applications, the most important being the manufacturing of Oxychloride or Sorel cement, pulp and paper processing chemicals, rayon and in the production of fertilizer and animal feed stuffs. Specially prepared light magnesium carbonate is used for the reinforcement and stiffening of rubber.

3.3.3 Prices

As is reflected by the prices, the magnesite markets are currently in oversupply. Price developments for magnesium compounds were mixed over the year 2003. Prices for dead-burned magnesia fell, whereas prices for magnesium chloride, magnesium sulphate and magnesium hydroxide increased. Prices of other compounds remained stable.
The quoted price for magnesium metal in Europe and the US remained virtually the same, but the price quote for China was increased by 300 $ per tonne. Table 5 compares prices of magnesium metal and a number of compounds at yearends 2002 and 2003.

Material and grade	**2002**	**2003**
magnesium metal, Europe free market	$1800-1900	$1850-1950
magnesium metal, China free market	1360-1380	1650-1660
magnesia, dead burned	428	402
magnesia, synthetic, 98% MgO	538	538
magnesium chloride, hydrous	320	353
magnesium hydroxide, powder, technical	991	991

Table 5: Price quotes of magnesium and magnesium compounds at yearends 2002 and 2003 (in US$ per metric tonne)

3.4 Possible application of the sequestration product

Magnesite is the foremost product of the sequestration process, when using olivine as a sequestration mineral. Application of the sequestration product will be a function of its quality, which in turn will be a function of the quality of the olivine used and the sequestration process itself.

From the previous pages it becomes clear that the use of the produced magnesium carbonate as such is limited in quantity and that other application will liberate the captured CO_2 again. Although, at first sight, this may seem contradictory to the purpose of mineral sequestration, it is not, for each tonne of CO_2 liberated form the sequestration product leaves a tonne of permanently fixed CO_2 in the ground in the form of non-mined magnesite.

If direct sequestration would be used, magnesite is a direct product of the reaction. However, if during pre-treatment Mg-hydroxide is formed as an intermediate product the whole sequestration process becomes redundant, unless one intends to dispose the sequestration product or re-use it as magnesite.

Aside from these considerations, very likely the magnesite produced through mineral sequestration will not be applicable to high quality uses. Refining will have to be done since the product may contain a considerable quantity of hydroxide and possibly metals and silica from the dissolution of the olivine. Therefore, application is most likely in the lower purity refractory and industrial grades.

4. SILICA

4.1 Introduction

Silicon is the second most abundant element in the earth's crust exceeded only by oxygen. It is only found as oxide (SiO_2 or silica) and as silicates, very rare other chemical forms are found in volcanic fumaroles.
The range of silica raw materials occurring in nature is quite extensive and includes relatively pure forms of the mineral such as rock crystal and vein quartz, SiO_2 in the form of unconsolidated sands, and as consolidated rocks such as quartzite and sandstone. In addition a wide range of synthetic or modified silica forms as cristobalite, vitreous silica, microsilica, and precipitated silica are used as raw materials for certain applications.
Quartz is the principal source of most silica products. Other sources are diatomaceous earth, tripoli, lascas and chert.
Quartz is characterized by:

- a density of 2.65
- a hardness of 7

4.2 Uses and qualities

4.2.1 General

Based on information provided by various governments, world production of industrial sand and gravel was estimated to be 95 Mt. The United States was the leading producer followed by Germany, Austria, France, Spain, Australia, and the United Kingdom, in descending order. Most countries in the world had some consumption and production of industrial sand and gravel, which are essential to the glass and foundry industries. Because of the great variation in reporting standards, obtaining reliable information was difficult.

Most important applications for silica are:

- Production of various types of glass
- Ceramics
- Foundry
- Ferro Silicon
- Silicon metal
- Silicon carbide
- Fluxes
- Silica brick
- Linings
- Fused silica

4.2.2 Glass

The specifications for silica for the production of glass are very well documented. All three characteristics (chemistry, mineralogy and physical properties) are of importance for determining when a silica sand is suitable for glass manufacture. First of all, the chemistry is most important dictating the minimum acceptable silica level and the maximum permissible impurity levels. Second is the mineralogy, which is mainly important for the naturally mined silica. The mineralogy can indicate whether an impurity is caused by the presence of a separate mineral, and thus removable, or an integral part of the silica itself. Finally, the physical size of the silica is critical to the manufacturing process employed in the production of different types of glass. Probably the most important criteria in the selection of glass sands are consistency and availability.

Flat glass

Most important for the production of flat glass, next to a high silica content, is that the silica content and thus the impurity level should be very consistent. Iron content should be low (preferred maximum of 0.1 %), and refractory minerals like kyanite, sillimanite and andalusite coarser than 0.4 mm should not be present, nor should there be any chromite coarser than 0.2 mm. A low and consistent alumina content is required preferably in the range of 0.2-1.6 %, and the variation not exceeding 0.1 %. A narrow size range should ensure uniform melting. Too fine a particle size is generally avoided to prevent carry over into the exhaust system.

Flint glass

Flint glass can be divided in three classes:

Grade A: Fine grade optical glassware.
Grade B: High grade domestic and decorative glassware.
Grade C: General colourless glassware, including containers.

In general, silica used for one of these three applications should be smaller than 20 mesh (850µm) and only 5 % should be smaller than 100 mesh (150 µm). More specifications are given in Table 6.

%	Grade A	Grade B	Grade C
Min SiO_2	99,5	99,5	98,5
Max Iron Fe_2O_3	0,008	0,013	0,03
Max TiO_2	0,03	NA	NA
Max Chromium Cr_2O_3	0,0002	0,0002	0,0006

Table 6: chemical specifications of silica for the production of flint glass

Coloured container glass

In this application the silica content is less critical than for the previous types of glass. Once again, consistency is of prime importance. For coloured glass the level of permissible iron is less stringent although it should not exceed 0,3% Fe_2O_3 for green glasses. In the manufacture of amber and brown glasses Fe_2O_3 contents as high as 1 % can be tolerated.

Fibreglass

Furnaces used in the production of the melt for fibre glass insulation (glass wool) and for continuous filament reinforcement fibre are not of the regenerative type. Consequently a fine particle size does not pose a problem. In fact, fine sands (silica flour) with 20 % reject on a 60 mesh (250 µm) screen, are used to promote ease of melting. Whilst optical clarity is not a requirement in glass fibre insulation too high an iron oxide content would affect heat transfer in the furnace. For glass fibre reinforcement the prime in manufacturing is a minimal number of breaks per hour. It is therefore important to eliminate any unmelted material, which would cause stoppages.

Ophthalmic glass.

Compared to optical glass the specifications for ophthalmic glass are less critical. However, a high silica content coupled with low levels of iron oxide and alumina remains required. The objects to be manufactured from one sheet of glass are small and therefore imperfections in the glass will result in only a small amount of wastage.

4.2.3 Ceramics.

Silica is incorporated in whiteware ceramic formulations sometimes in amounts representing as much as 40% of the ceramic body, with the exception of bone china in which it is not used at all. The addition serves to provide whiteness, render the body easy to dry, and provide compatibility between the body and the glass to prevent crazing or pealing. Because silica represents a low value/high bulk commodity, manufacturers tend to compromise their specifications according to what is locally available. Main sources of sand in this application are silica sand, calcined silica sand, and calcined flint. In addition to being used in the ceramic body, silica in the form of flour is used in enamels and frits. For use in enamels silica flour produced by fine grinding of quartzite, sandstone or lump quartz should contain more than 97,5% silica, less than 0,55% alumina, and less than 0,2% Fe_2O_3.

In order to ensure high whiteness of the ceramic body, the silica in the formulation should be low in iron. Purity and small particle size (BS mesh 200) are fundamentally important for silica incorporated in ceramics. Although alumina is added separately to the batch its presence in silica sand is restricted thereby allowing the total content to be more easily controlled.

4.2.4 Foundry.

Silica is used for foundry applications because of its resistance to thermal shock. It is used in foundry cores and moulds. Grain size and shape are more important than chemical purity although for iron casting a minimum silica content of 85% is required whilst in steel foundries the content should at least be 95%. The cost per tonne of casting is largely determined by the amount of binder required. This amount is related to the grain surface of the foundry sand. A coarse sand will have a low surface area, thus requiring less binder than a fine sand. Rounded grains consume less binder than angular particles with a higher surface area. The silica precipitated during the neutralization of acid with olivine forms very fine clusters like bunches of grapes. The individual grains range in size from 10 to 50 nm. It is unlikely that this silica is suitable for foundry applications.

4.2.5 Ferro-silicon

Ferro-silicon is produced by smelting a mixture of quartz, metallic iron, and a reducing agent such as coal, charcoal or wood chips. The grade of ferro-silicon produced is controlled by varying the proportion of metallic iron. Ferro-silicon is produced in six grades containing between 20% and 95% silicon.

Generally ferro-silicon manufacturers prefer quartz as their raw material silica source, although quartzite can also be used. When crushed these yield strong and competent lumps and particles in which the individual grains and crystals are sufficiently well bonded to withstand electric arc furnace smelting without thermal or physical decomposition or breakdown above the arc reduction zone. Regarding the above mentioned description of the raw material feed it is unlikely that precipitated silica from carbon dioxide sequestration can be applied without any pre-treatment.

Ferro silicon is used for heavy media separation and atomization. Ferro silicon is also widely used in casting, melting and related metallurgy industry. It can be used as basic materials for adjusting, inoculation, suspending, coating and de-oxidization in steel melting, casting, mineral processing and melting rod industry. It is also used for production of semiconductor pure silicon in electric industry and silicon copper in chemistry industry.

4.2.6 Silicon Metal

Production of silicon metal is similar to that for ferrosilicon except that no iron is added and raw materials are required to be low in contaminants. Generally a high purity quartz, containing about 99,8% SiO_2, is selected. The alumina and iron contents are also generally specified to be below 0,1% with calcium and phosphorous contents restricted to 0-0,005%. Silicon metal is graded according to the iron content. A final product grade of 0,35% iron would require an initial iron content in the quartz of 0,05%. Some manufacturers are also producing higher grade silicon metals with final iron contents of around 0.25% Fe_2O_3. About 2.6 tonnes of silica is consumed to produce 1 tonne of silicon metal.

4.2.7 Silicon carbide

Silica is used as a raw material for the production of siliconcarbide (SiC). SiC is synthesized through a variation of the original Acheson process where sand and coke are reacted in a resistance furnace. High quality silica sand (min 99,5 % SiO_2) and a carbon source are subjected to electrofusion at 2.100-2.400°C in a trough-like furnace with carbon electrodes at each end. The process can take between 36 hours to 20 days to complete, although most commercial production has a reaction time of around two or three days. The reaction requires 2,3-3,2 kg of raw material to produce 0,40-0,45 kg SiC.

The world production capacity is estimated at 1,1 million tonnes of silicon carbide of which ± 40% is held by China. The actual production is estimated in the region of 750-850,000 tpa.

There are three main markets for SiC. These are the abrasives, the refractory and metallurgical markets. Other markets are the advanced ceramics and electronic markets, the latter using the highest grade, green SiC. The world market for SiC is estimated at a value of US$ 670 million for a volume of 600-700,000 tpa. Metallurgical end use comprises the bigger part of the market followed by abrasive and refractory applications. The USA and Europe account for approximately 70% of the market, the Pacific Asia for the bigger part of the rest.

Abrasives

SiC is an extremely hard and wear resistant material making it ideal for abrasive applications. Abrasive grade SiC is often used as macro and microgrits. Heavy duty requirements require a compact and cubic grain while a splintered grain is best suited for low duty applications.

SiC refractory applications

SiC is used in refractories as a result of its resistance to thermal shock and attack by a wide range of chemicals as well as being able to withstand a wide range of temperature conditions. Although the overall refractories market is experiencing a decline in volume and demand, as far as SiC is concerned the increasing demand for products with longer service lives has meant that SiC has fared better than many other raw materials.

Metallurgical applications

SiC used in metallurgical applications represents the lowest quality grade of SiC, typically 65-92% SiC content. The SiC is used either as loose grains or as briquettes. It is used as an alloying element, replacing the carbon ferro-silicon combination due to its relative purity and high stability in oxidant atmospheres. It is also used as a de-oxidant in molten iron and steel.

Minor applications

The advanced ceramics market consists of four main sectors, coatings, chemical and environmental, structural and electronic. For these applications the highest grades SiC are used. The electronics market is the largest and represents 70% of the global advanced ceramics market.

4.2.8 Fluxes

Silica in the form of massive quartz, quartzite, sandstone and unconsolidated sands is used as a flux in the smelting of base metal ores where iron and basic oxides are slagged as silicates. The silica is used to balance the lime/silica ratio of the blast furnace burden. Because free silica is the active slagging agent the silica content should be as high as possible (above 90%), although the actual level does not appear to be critical. Additionally, minor amounts (max 1,5%) of impurities such as iron and alumina can be tolerated. Generally lump silica in the size range of 0,8 to 2,5 cm is used in this application.

In more specialized applications, e.g. as a fluxing agent in welding fluxes, the silica is added in the form of flour or as diatomaceous earth. Here size requirements are consistent with the requirements of the final product. For coated electrodes the particle size must be such as to aid extrusion, provide a coating sufficiently tough to withstand mechanical damage from conveyors and brushing units, and produce a pore structure which allows immediate continuous drying without excessive cracking. Generally the particle size should not exceed 250µm with an average size of 60µm for standard electrodes. The particle size for the manufacture of agglomerated fluxes (used in submerged arc welding) should be less than 60µ to ensure even distribution of all constituents and for flux cored wires should be smaller still. Chemical considerations are more complex because of the interaction between the large number of constituents in a welding flux. However phosphorous and sulphur cannot be tolerated in any formulation because they cause cracking, whilst lead, zinc, arsenic, antimony, boron, cadmium, and vanadium are undesirable since they affect the fluidity of the slag and reduce ductility of the weld metal.

4.2.9 Hydraulic Fracturing

Sand grains are used to stimulate oil well production. A sand containing fluid is pumped under high pressure into the pay zone of the production well. As soon as the fluid is pumped away the grains remain to keep the cracks in the reservoir open. In this way the oil and gas can move freely towards the well. It is very unlikely that this application is suitable for the precipitated silica from carbon dioxide sequestration.

4.2.10 Silica brick

Silica bricks have been used as liners in the production of steel and base metals but are now largely replaced by bricks made of magnesite, dolomite or alumina. However, thanks to its excellent load resistance at high temperatures silica brick continues to be used in coke ovens, ceramic kilns, glass tank crowns, as chequers in the regenerators of some glass tanks, and as blast furnace chequers in some steel mills.
The prime requirements for the raw materials incorporated in refractory bricks is that they should maintain the desired degree of physical and chemical identity at high temperatures in addition to which they should exhibit resistance to abrasion, impact, thermal shock, and a high load level. The chemical requirements for silica for use in refractory brick demand a minimum SiO_2 content of 97% and preferably greater than 98%, Al_2O_3 less than 1% and preferably less than 0,5%, and total alkalies less than 0,2%. For super duty bricks a total content of alumina, titania, and alkalies should be no greater than 0,5%.
Factors other than chemical purity also affect the performance of silica bricks. To prevent expansion during use, a high conversion of quartz to cristobalite or tridymite is required and to ensure adequate transformation, the bricks are fired in batch kilns at a temperature above the conversion temperature of 1.470°C for long periods to attain densities of 2.3-2.35. To speed up the conversion process and thereby reduce energy consumption, chalcedonic silica can be added. Alternative lime and iron oxide assist the conversion to cristobalite and tridymite respectively. Porosity, which can be controlled by particle size, also determines the effectiveness of the brick. Low porosity is necessary

to ensure a long working life. The porosity of the refractory brick can be controlled by the particle size distribution of the feed. The following distribution would be consistent with a low porosity brick: 45% coarse (0,5-3,35 mm), 10% medium (0,18-0,5mm), and 45% fine (flour - 0,18mm).

4.2.11 Linings

Many types of natural stone are used as linings for ball and pebble mills, but by far the majority of these are silica-based containing more than 96% silica. The crystalline structure of these rocks is of prime importance in these applications, more specifically crystal size and degree of interlocking of the crystals. Precipitated silica is not very likely to be a suitable raw material for this application.

4.2.12 Fused Silica

High purity sand deposits provide the raw material for bulk refractory grade fused silica, which is electric arc melted at extremely high temperatures. Optical and general purpose fused silica rods and tubing (99,4-99,9% SiO_2) are drawn from a melt made from high purity chemicals. Fibre optic purity is made by thermal decomposition of high purity gaseous silica containing chemicals. The glass may be clear or translucent, in which case it is often referred to as fused quartz. The glass has very high viscosity, and this property allows the glass to be formed, cooled and annealed without crystallizing. Fused silica glass is a very low thermal expansion material, and so is extremely thermal shock resistant. The material is also chemically inert up to moderate temperatures except to hydrofluoric acid, which dissolves silica. It will de-vitrify above about 1100°C in the presence of contaminants such as sodium, phosphorus and vanadium, with the formation of cristoballite crystals which destroy the properties of the glass. The dielectric properties are stable up through gigahertz frequencies.

Fused silica has a purity of at least 99,8%, trace impurities significantly affect the performance of the material in critical applications. Commercially available vitreous silicas have an impurity content of less than 1.000 ppm. Originally, transparent vitreous silica could only be produced from natural quartz since it was found that the gas contained within silica sand produced bubbles within the fused silica thereby producing a translucent or opaque material. Bubbles also introduce structural weakness within the product and pose problems of gas entrapment. However, the availability of lower cost high purity sands (especially those obtained as a floating by-product) has caused manufacturers to turn away from quartz crystal with its rather more restricted availability and higher cost. Increasingly manufacturers are converting their furnaces to be able to handle finer particles that require less energy in melting.

Component	Opaque	Transparent
SiO_2 %	99,8%	>99,95%
Fe_2O_3 ppm	70	0,9
TiO_2 ppm	100	0,5
Al_2O_3 ppm	200	18
CaO ppm	40	1,2
MgO ppm	11	0,2
Na_2O ppm	25	1,9
Li_2O ppm	5	0,7
Cu.Ni,Co,As ppm	<1	< 1

Table 7: Typical analyses for silica feed for vitreous silica.

Transparent vitreous silica in the final product must have a purity of more than 99,95%, should be free from all inclusions and mist specks greater than 0,01 mm^2 in diameter. Transition metals like Cu and Mn can cause fluorescence. The presence of alkalis causes long term stability problems due to de-vitrification by forming silicates. In addition they reduce heat resistance. For translucent vitreous silica raw material must be capable of purification to a maximum impurity level of around 300 ppm, and for transparent silica it should be purified to a maximum of about 30 ppm.
Particle size for the silica feed is very much dependent upon the fusion methods and sand ranging from 50-500µ can be used.

4.2.13 Microsilica

Microsilica is essentially formed as a by-product from the ferro-silicon or silicon production. Miniscule spheres of SiO_2 are formed in the upper part of the furnace where the SiO vapour mixes with oxygen. The average particle size formed is 0,15 micron. The microsilica formed from the production of ferro-silicon is less pure (85-90% SiO_2) than that from the production of silicon (94-98% SiO_2). About 120,000 tpa of high quality microsilica is available for use. Its small particle size and high specific surface make microsilica a highly reactive product. Because of their size and shape, particles are able to move between and around coarser particles, filling even the most minute space in any mixture. In these pores they react with the last bits of unreacted calciumoxide and water to form a very dense structure. Another advantage is that, by filling up the pores, less water and cement is needed in the mixture. Concrete made with microsilica is less vulnerable to chloride penetration and freeze-thaw stress. The higher qualities microsilica are used for the production of refractories.

Component	Refractory grade	Concrete grade
SiO_2	94-98	85-96
Fe_2O_3	0,1-0,4	0,2-3,0
Al_2O_3	0,02-0,4	0,2-0,5
CaO	0,1-0,4	0,1-0,7
MgO	0,2-0,9	0,3-3,5
Na_2O	0,1-0,4	0,2-1,8
K_2O	0,2-0,7	0,4-3,5
C	0,2-1,3	0,4-2,3
LOI	0,05-2,5	0,7-4,0

Table 8: Typical chemical composition of microsilica

Other types of microsilica are fumed silica, which is produced from hydrochloric acid and ferrosilicon, and precipitated silica, obtained from the reaction of water glass and sulphuric or carbonic acid. Fumed silica has a large disadvantage compared to the microsilica from ferrosilicon production since it is four times more expensive. The water glass is produced by heating 99% SiO_2 with caustic soda. After mixing with acid the silica is precipitated by dilution. The size requirement for the product formed is 100% less than 20 mesh (850μm).

4.2.14 Filler and extender applications, precipitated silica

Silica in its finest forms, as a flour, microsilica, precipitated and fumed, finds application in reinforcement filler and extender applications. Here the particle size and surface area of the silica are two of its most important attributes. Precipitated silica is composed of aggregates of sub micron particles (average diameter 0,019μm) which agglomerate to form larger clusters. Silica content of the grades varies from 87% to 97,5%. Fumed silica also found in the agglomerated form, has particles with nominal diameters ranging from 0,007 to 0,014 μm and a silica content averaging more than 99,8%.

Plastics

Silica flour is used to impart flexural and compressive strength to plastics. In addition, their low oil adsorption, wettability, and rapid dispersion allow high loading in most compounds. Silica additions improve dimensional stability and improve resistance to thermal shock. One problem identified with the use of these products, however, is wear on extruding nozzles and moulds. It is anticipated that finer gradings should overcome this draw back.

Precipitated silica accounts for only 2 % of the total mineral consumption in plastics (1999), it has however shown a tremendous growth during the 80's. This growth was mainly due to the increased use of precipitated silica in tyres. Precipitated silica is a critical product for battery separator producers, the performance of the silica determines the performance of the separator. Most of these separators are used in automotive batteries. Precipitated silica is produced in Europe by such companies as Degussa AG, Rhone Poulenc, AKZO Nobel Chemicals BV, Huber and PPG Industries.

Grade	Reinforcement Product	Flatting agent
Surface area (m^2/g)	60	180
pH (5% in water)	8,0	6,5-7,3
Specific gravity		2,1
Refractive index	1,44	1,455
Oil adsorption (kg/100 kg)		210
SiO_2	92%	97,5%
CaO	0,8%	0,5%
Fe_2O_3	0,53%	0,1%
Al_2O_3		0,6%

Table 9: Typical properties of precipitated silica

Silica gel is really a niche product in plastics applications accounting for less than 1% of the total volume of minerals used in plastics. Micronised silica gel is used as an anti blocking agent in specific film applications and is primarily used in Europe.
W.R. Grace & Co and Crosfield Chemicals are the main suppliers and Degussa is also offering a competing precipitate.
Fumed silica also accounts for less than 1% of the mentioned mineral market. Fumed silica is used in unsaturated polyester resins and in PVC plastisols. The primary function of the fumed silica in unsaturated polyesters is to provide thixotropy in such applications as laminating resins, gel coats and putties. In PVC plastisols, fumed silica is also often used in small amounts to help regulate the viscosity. Fumed silica is produced in Europe by Degussa, Cabot and Wacker Chemie GmbH.

Grade	M-5	M7-D	H-5	EH-5
Particle size (μ)	0,014	0,014	0,007	0,007
Surface area (m^2/g)	200±25	200±25	325±25	390±40
pH	3,5-4,2	3,5-4,2	3,5-4,2	3,5-4,2
Specific gravity	2,2			
Refractive index	1,46			
SiO_2 (%)	99,8 min			
Colour	white			

Table 10: Typical properties of Cab-o-Sil fumed silica

Paint

As a filler and extender in paint formulations silica in the form of flour serves to render the paint more resistant to chemicals because of its acid resistance and, because of its hardness, scrubbing and wear resistance of surface films are also enhanced. The addition of silica also adds tint retention, durability and flowability. Fumed silica can be used as a thixotropic agent in paints.

4.2.15 Grinding and abrasion

Quartz used to be a very attractive mineral for grinding and abrasion due to its hardness (7 on Moh's scale) and conchoidal fracture. Nevertheless it has lost most of it market share because of the tightening legislation governing the use of free silica in the atmosphere. Silica flour is used as an abrasive agent in soaps and scouring pads.

4.3 Possible application of the sequestration product

The silica produced in mineral sequestration of CO_2 will be a fine precipitated silica. Because of its fineness some of the possible uses discussed in the previous chapter must be disqualified immediately on account of the constraints put on the physical qualities of these applications. For example it is unlikely that precipitated silica can be used for hydraulic fracturing, as cores or moulds in foundry applications or in linings and in the production of ferrosilicon. Either its lack of crystallinity or its extremely fine grain size makes precipitated silica unsuitable for these applications. In the production of most glasses the grain size of the silica source is also important. A possible use here would be in the production of fibreglass insulation.

The potential use of the sequestration product in the market for precipitated silica and microsilica in fillers and extenders or in very fine grained flour applications is obvious. In the remaining potential uses the required physical properties are such that replacement by the sequestration silica could be considered provided that the chemical quality is sufficient.

Application of sequestration silica for the production of silicon and silicon carbide other than metallurgical and the production of welding fluxes seems virtually excluded on account of the extremely high quality that is required for these uses. Also these uses do not account for great quantities and are therefore less interesting. The same applies for fused silica. World consumption of silica for this application is in the order of 1 million tonnes.

Obvious applications are in the field of microsilica and in the market for fillers and extenders. Possible applications are the replacement of sand in the production of fibreglass and ceramics and for metallurgical fluxes. The latter use will require considerable agglomeration of the silica to lumps in the order of 1-2 cms.

Table 11 on the next page gives an overview of potential uses and the corresponding chemical and grain size restrictions.

Potential use	**Grade**	**Grain size**		**Minimum SiO$_2$ content %**	**Maximum impurities %**
		Minimum	**Maximum**		
Fibre glass			20% > 250µm	.	
Ceramics			75 µm	97,5	0,55% Al2O3 0,2% Fe$_2$O$_3$
Silicon				99,8	0,1% Al, 0,1% Fe 0,005% Ca 0,005% P
Silicon carbide	metallurgical			65-92% SiC	
	other			99,5	
Fluxes	metallurgical	0,8 cm	2,5 cm	90	total 1,5 %
	electrodes		250 µm	90	1,5 %, no P,S, Zn, As, Sb, B, Cd, V
Refractory bricks				97	Al$_2$O$_3$ 1% alkalies 0,2%
Fused silica		50 µm	250 µm	99,8	total 0,1%
Microsilica	from ferro-silicon	0,15 µm average		85-90	
	from silicon			94-98	
Fillers, extenders	precipitated	0,019 µm average		87-97,5	
	fume	0,007 µ	0,014 µm	99,8 (avge)	

Table 11: Overview of potential uses of precipitated silica from CO$_2$ sequestration.

4.4 Prices and markets

4.4.1 Prices

Prices for several types of silica are given in Table 12. These prices were valid in 2002 and are only indicative.

Silica application	Price in US$/ton
Industrial sand (metallurgical flux)	12
Industrial sand (ground fillers)	83
Fillers for paint, putty, and rubber	83
Foundry moulding	83
Swimming pool filters	77
Well packing and cementing	65
Municipal water filtration	42
Fibreglass	41
Abrasives	37

Table 12: Price indications of silica for several applications in US$ (U.S. Geological Survey, Mineral Yearbook 2002)

4.4.2 Fused Silica Market

The USA leads the production of fused silica, and is home to the two biggest producers: C-E Minerals and Minco Inc. Estimated capacity of these two companies is over half the world production of some 200.00 tpa (IM april 2001).

The three markets for fused silica are electronics, investment casting and refractories. Electronics is by far the biggest consumer with around 70% of the total. Fused silica has extremely good dielectric and insulating properties, and is used as an inert, low expansion filler for epoxy resins and electronic circuits. The investment casting industry forms the second biggest market with 10-20% of the total. Fused silica is used in the refractory casting slurry, where it coats a wax replica of the component to be cast. The refractory stucco is fired and molten iron is poured into the mould. Finally, the fused silica shell is knocked out. Fused silica makes this 'knock out' stage easier than other refractories like zirconia and aluminosilicates. The refractory industry accounts for another 10-15% of the market. Fused silica bricks are mostly used in glass production and in the construction of coke ovens. This market has not witnessed any growth because of the overall reduction in specific consumption of refractories, and a growing preference for alumina and carbon based bricks. Silica refractories can also be made from non fused silica, where quartz is fired to stabilise the SiO_2. Prices range from $260-360 per ton depending on the quality.

4.4.3 Market outlook silicon carbide

The SiC market is characterized by the potential of oversupply, but this is being tempered by the high cost of production associated with the large amounts of energy required to produce SiC, and increasingly stringent environmental measures related to the burning of coke and subsequent sulphur emissions. Growth is expected in the abrasive market and most of all in the advanced ceramics market.

5. IRON OXIDES

5.1 Introduction

When using olivine as sequestration mineral, iron oxides will be among the products resulting from the sequestration process. The magnesium-rich end member of olivine generally contains some 5-10% FeO. The iron will dissolve and remain in solution as Fe^{2+}. After precipitation of the silica-gel and under normal oxidizing conditions the dissolved iron can be precipitated as an amorphous oxy-hydroxide upon increasing the pH of the solution to around 5. Through drying and heating to temperatures above 140°C, the hydroxide may be converted to hematite (α-Fe_2O_3).
Under normal oxidizing conditions with air and a pH of 6-7, goethite (α-FeOOH) and lepidocrocite γ-FeOOH) will be formed. Under special conditions (slow oxidation and $pH \geq 8$) dissolved iron can be precipitated as magnetite (Fe_3O_4). This will facilitate separation of the solid and liquid fractions, but requires a somewhat cumbersome processing.
Since olivine generally contains a certain amount of Ni, Mn and Co these elements will enter into solution and will partially precipitate with the iron oxides. A typical nickel content of olivine is 0,3 %. As a result the oxide precipitate may contain some 2 % of Ni. Mn-content will be of the same order or slightly less.

5.2 Uses and qualities

5.2.1 General

Each tonne of CO_2 sequestered may generate 55-110 kg of Fe_2O_3 or 53-106 kg of Fe_3O_4.
The major uses of iron oxides are:
- as an ore of iron;
- in pigments and paints;
- as catalysts

The quality requirements for these applications vary enormously. With respect to the iron oxide content this may vary from as low as 40% in some natural ochres used as pigment to more than 99,5% for oxides used for the production of magnetic pigment. Requirements for oxides used in the production of ferrites for magnetic materials can even be more stringent. Iron oxides used for the production of iron and steel should contain at least 60% of iron in oxide form, i.e. 85% of Fe_2O_3.
The use of catalyst and other specialty applications require a high purity product. Since it is not likely that such qualities will be produced by CO2-sequestration, these applications will not be further discussed here.

5.2.3 Iron ore

Raw or pig iron is made by reduction of iron ore in a blast furnace. The raw iron is then reprocessed to steel in an electric arc furnace or in a basic oxygen furnace. Scrap and DRI (Direct Reduced Iron) can also be fed to the electric arc furnace.
Virtually all iron ore is composed of iron oxides. The bulk of these ores consists of trivalent oxides, but magnetite is also used as a resource for production of steel. In order to qualify as a useful resource the material must have an iron content of 60% or more corresponding to 85% or more Fe_2O_3. Chemical constituents that lower the value of the ore are silica and alumina, moisture and certain metal impurities like zinc. On the other hand, substances like limestone and dolomite ($CaCO_3$ and $CaMg(CO_3)_2$) increase the value of the ore, since they have to be added in the processing of the ore anyways.
Another important aspect is the grainsize of the material. Lumpy material can be fed directly to the blast furnace, whereas fine material needs to be sintered before entering the furnace.
The normal blast furnace offers some flexibility with respect to the quality of its feed, so that lower quality ore can also be used. However, the production of Direct Reduced Iron generally requires premium qualities and is very sensitive to fines.

5.2.4 Pigments

Both natural and precipitated iron oxides are extensively used as pigments. The advantages of iron oxide pigments are their high tinting strength and stability. They are highly resistant to acids and alkalis.
Until the beginning of the 20th century the need for iron oxide pigments was fulfilled by natural oxides. Since then precipitated iron oxides have captured an increasing share of the market. One of the main reasons for this is that precipitated oxides can be produced within a narrow range of specifications, both with respect to particle size and chemical composition (purity). Synthetic oxides are generally precipitated from ferro-salt solutions under oxidizing conditions.
The trivalent (oxy-)hydroxides generally produce yellow, brown and red pigments, magnetite is black. Magnetite and maghemite (γ-Fe_2O_3) are used as magnetic pigments for data recording. This application requires a high purity oxide (> 99,5% Fe_2O_3) and it is unlikely that the precipitation product from mineral sequestration will satisfy this requirements. The presence of other metals can be detrimental to the magnetic properties of the oxides unless added in specific quantities. Moreover, the market for magnetic pigments is rather small and in the order of thousands of tonnes only.
Yellow, red and brown pigments are mainly used in the construction industry for colouring concrete products, asphalt, tiles and bricks and in coatings. Minor applications include the colouring of plastics and rubber.
The purity requirements for iron oxides used in pigments vary strongly. The oxide content of yellow pigments is generally lower than for red and brown colours. For example, in natural ochres the oxide content may be as low as 20 to 50%, whereas oxide pigments produced by Bayer contain from 80-97% iron oxide. For each type of pigment the oxide content varies within a range of only 1 to 3%. The sum of SiO_2 and Al_2O_3 contents varies from 2-4% for red and brown pigments, but should not exceed 0,2 % for certain types of yellow (Bayer, Technische daten anorganische Pigmente).
Table 13 summarizes the iron content of some natural iron oxide pigments.

Colour	Name	Fe2O3 content %	Main source
Yellow	Yellow Ochre	10-20	Southern France South Africa
Red	Haematite	70-99	Spain, USA, South Africa
	Spanish Red		
	Red Ochre	55-60	USA
Medium-dark yellow	Sienna	50-60 (1% MnO2)	Cyprus, USA, Italy
Red/orange	Burnt Sienna		Cyprus, USA
Greenish gray/brown	Raw Umber	20-50 (5-20% organics and MnO2)	Cyprus, USA

Table 13: Iron contents and sources of some natural iron oxides

5.3 Markets and prices

5.3.1 Introduction

The markets for iron oxides used for pigments and for iron ore are completely different. The size of the iron ore market is about three orders of magnitude larger than the pigment market.

Although the chemical composition of the different raw materials may overlap, the iron ore market prefers a lumpy and hardened material, whereas the pigment market prefers fines. Production of pigments often includes wet processing. On the other hand, iron ore needs to be as dry as possible.

Mining techniques are also different. Where iron ore mining uses large low cost bulk mining techniques, the winning of pigment ores is small scale and much more selective. An important factor in the production of pigment is also the need to produce a consistent and stable colour. As a result the prices for various grades of iron oxides used for pigments are considerably higher than those for iron ore.

5.3.2 Iron ore

The total world mine production of iron ore in 2004 amounted 1 250 Mt (million tonnes). World resources are estimated at some 800 000 Mt.

The largest producers of iron ore are China, Australia, Brazil and India all producing over 100 Mt/y. Crude steel production in 2003 amounted to 965 million tonnes for the 61 countries reporting to the International Iron and Steel Institute. At the present rate of steel consumption world resources would be sufficient for some 700 years. However, crude steel production has been rising in the last couple of years. Production rose from 904 million tonnes in 2002 to 965 million tonnes in 2003. Also recently production

figures rose with China reporting the strongest growth figure of 24,3% (Jan 2005 compared to Jan 2004). As a result the price of scrap has also increased.
Table 14 gives an overview of the main producers of crude steel and their iron ore output. The table also lists some relevant steel producers with no iron ore resources of their own.

Country	**Annual crude steel production (2003) in million metric tonnes**	**Annual iron ore output (2003) in million metric tonnes**
China	220	261
Japan	110	<10
United States	90	46
Russia	63	92
South Korea	46	<10
Germany	45	<10
Ukraine	37	62
India	32	106
Brazil	31	212
Italy	27	<10
France	20	<10
Taiwan	19	<10
Turkey	18	<10
Spain	17	<10
Canada	16	31
Mexico	15	11
United Kingdom	13	<10
Belgium	11	0
Australia	7,5	167
Netherlands	6,6	0

Table 14: Annual crude steel and iron ore production of selected countries in 2003 (USGS Mineral Commodity Summaries, Intern. Inst. of Iron and Steel 2005)

The price of iron ore depends on its chemical quality, but the physical characteristics play also a role. Lumpy ore commends a higher price than fine grained material. In general, the selling price of ore is controlled by long term contracts and is not disclosed to the public. Any figure published must therefore be considered as indicative only.
In 2003 the average FOB (free-on-board) value of iron ore shipped in the United States was US$ 26,86 per ton. In that year iron ore prices rose worldwide.

5.3.3 Pigments

The worldwide production of iron oxide pigments in 2002 was in the order of 1,5 million tonnes. Of this amount 26% was supplied by China, 25% by Western Europe, 22% by India 15% by Japan and 11% by the United States.
India is by far the largest producer of natural oxides with 365 000 tonnes of ochre in 2003, followed by Spain with 70 000 tonnes of ochre and 15 000 tonnes of red oxide.
The price of iron oxide pigments varies widely, with thousands of dollars per tonne being paid for good quality magnetic pigments. Red and yellow oxide pigments fetch from 200 to 2000 US$ per tonne.

Quality	Delivery mode	Price	Source
Spanish ochre	FOB Spain	125-135$/tonne	IM june 2002
Ochre	FOB Cartersville	370-460$/tonne	IM june 2002
Synthetic black	FOB USA	2070$/tonne	USGS Min. Yearbook 2003
Synthetic yellow	FOB USA	2250-2340 $/tonne	
Natural buff	FOB USA	1160-2014 $/tonne	

Table 15: Prices of some natural and synthetic iron oxide pigments
(IM = Industrial Minerals)

5.3.4 Nickel

The nickel content of dunite should not be forgotten in an economic appraisal of mineral sequestration. Dunite commonly contains a few tenths of one percent of nickel as part of the olivine structure. This means that each tonne of CO$_2$ sequestrated could generate a few kilograms of nickel either in the iron containing solution or as part of the residue. The current price of nickel is high and stood at 14 600 US$/tonne at the beginning of February 2005 at the London Metal Exchange (Mining Journal, 2005).

5.4 Possible application of the sequestration product

From a compositional point of view iron oxides produced by mineral sequestration can be used both as an primary material for the production of iron as well as for the production of pigments, provided some basic treatment, such as drying is performed. When using dunite as a sequestration material, in the order of 0,1 tonne of iron oxides will be produced for each tonne of CO$_2$ sequestered. A 600 MW coal fired power plant will use some 4 million tonnes of dunite for full CO$_2$ sequestration and, theoretically, produce 40 000 tonnes of iron oxides. Such an amount would completely disturb the pigment market for iron oxides on a national scale and would even severely disturb the European market.

The situation for application of the sequestration product as a primary material for the production of iron is quite different. The Netherlands consume in the order of 10 million tonnes of iron or per year. A quantity of 40 000 tonnes is easily adsorbed provided that the quality is good.

6. ALUMINIUM HYDROXIDE

6.1 Introduction

In case anorthite is used as a sequestration mineral, Al-hydroxide may be produced. In comparison: bauxite, the main resource of aluminium, contains 40 to 60% of aluminium oxide versus 35% in pure anorthite. Not surprisingly, anorthosite has therefore been considered as a source of aluminium in the past. For example, the 1985 edition of the United States Bureau of Mines Bulletin Mineral Facts and Problems (No. 675) is quoted as follows:

> *"Although bauxite is now the main source of aluminum, other aluminum resources such as kaolinitic clays, nepheline syenite, anorthosite, and alunite may become important sources in the future....... Development of improved techniques for processing of these alternate aluminum sources will hasten their utilization as a basic aluminum supply source. The United States has large resources of such materials and could meet most of its alumina raw material raw materials needs indefinitely if the technology is developed."*

Although nepheline has been used as an aluminium resource in the former Soviet Union, no technique to extract the metal from anorthosite has been developed yet.

6.2 Resources, uses and qualities

6.2.1 General

The processing of bauxite ore involves washing, screening and drying of the raw bauxite. The material is then submitted to a caustic leach at elevated temperature and pressure, the so-called Bayer process. In the Bayer process the aluminium is separated as a sodium aluminate solution from impurities such as iron and titanium oxides and silica. The insoluble residue is termed red mud.

The sodium aluminate solution is seeded with alumina trihydrate crystals to precipitate, upon cooling, alumina trihydrate or ATH ($Al_2O_3.3H_2O$) from the super saturated solution. The precipitate is washed and calcined for the production of aluminium metal and minor quantities of high grade abrasives and refractories. A portion of the alumina may be left in trihydrate form for further use as a chemical. Specialty applications of ATH include water treatment, and the production of flame retardants, zeolites and molecular sieves, catalysts and adsorbants, and aluminium fluoride.

6.2.1 Bauxite

World bauxite resources are in the order of 55 to 75 billion (10^9) tonnes. The largest resources occur in Africa (Guinea), Australia and South and Central America (Brazil, Jamaica).

Bauxite contains 40 to 60% of aluminium oxide. Fe_2O_3 contents of bauxite may range up to 20% especially in the Jamaican type bauxites. The aluminium oxide is mostly present in hydrated forms, such as $Al_2O_3.3H_2O$ (gibbsite) and $Al_2O_3.2H_2O$ (boehmite). Consequently, hydrate water may be in the order of 50 % of the Al_2O_3 content. Iron oxides may also partly occur in hydrated form.
Free water in bauxites may range between 5-30%. This can be removed by drying to around 300°C. Hydrate water is removed by heating to about 930°C (calcination). Some typical dry bauxite compositions are given in Table 16.

Country	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	TiO_2 %
Jamaica	45-49	17-22	0,8-8	2,5
Guyana	55-60	<3	2-5	
Brazil*	55	11	3,5	
Guinea	57-60	2-4	<1	
Queensland (Australia)*	53-58	12	4-7	
Darling Range (Australia)	38-46	11-16	10-23	4

Table 16: Typical oxide composition of some dry bauxites
* = after benificiation, (washing, screening)

In 2004, total world mine production of bauxite amounted to 156 million tonnes. After some benificiation, such as washing, screening and drying, 85% of this amount is used for the production of aluminium by way of the Bayer process. 10% of all mined bauxite is converted by some purification and calcining to alumina for non-metal uses mostly refractory applications, cement, abrasives and chemical uses. A further 5 % is used for non-metallurgical specialty applications. For example, bauxite is used as an additive in the production of mineral wool in order to increase the Al-content of the furnace feed and thereby to improve the viscosity of the smelt.

6.2.3 Refractory and abrasives

Refractory and abrasive products are either derived from special grades of bauxite or from ATH. Processing for abrasives may include fusion in electric arc furnaces up to 2500°C. The fused alumina derived from ATH (WFA or White Fused Alumina) has a higher grade than the product derived from bauxite (BFA or Brown Fused Alumina). Whereas WFA may have a purity of 99,7 % Al_2O_3, BFA only contains 80-88 % Al_2O_3. Table 17 gives a comparison of dried bauxite composition and refractory and abrasive grades used for the production of BFA amongst others.

Component	Metal grade dried Jamaican	Refractory grade (calcined)	Abrasive grade (calcined)
Al_2O_3	47,0*	86,5*	83,0*
SiO_2	3,0	7,0	6,0
Fe_2O_3	22,0	2,5	8,0
TiO_2	3,0	3,75	3,0-4,5
K_2O+Na_2O	ns	0,2	0,7
MgO+CaO	ns	0,3	ns
CaO	ns	ns	0,2
MgO	ns	ns	0,4
MnO_2+Cr_2O_3+V_2O_5	2,0	1,0	1,0
P_2O_5	1,5	ns	0,5
Loss on ignition	ns	0,5	1,0

Table 17: Typical specifications for grades of bauxite
(in wt%, * denotes minimum value)

6.2.4 Production of aluminium

Roughly 85 % of all the bauxite mined in the world is used for the production of aluminium metal. The process involves calcining of ATH (aluminium trihydrate) to alumina and subsequent electrolytic reduction of the alumina in a molten bath of cryolite.

The minimum Al_2O_3 content of bauxites currently processed is in the order of 40 %. The maximum silica (SiO_2) content is 8%. A higher silica content results in too much loss of alumina and solvent liquor in the refining process. Inferior bauxites with silica contents as high as 15% may be treated by way of the so-called combination process, but, evidently, these ores command a lower price.

6.3 Markets and prices

6.3.1 Markets

Over the last decennium the world mine production of bauxite has gradually increased from 106 million tonnes in 1994 to 156 million tonnes in 2004. Of this amount 95 % or some 150 million tonnes were converted to alumina (Al_2O_3) by way of aluminium trihydrate for the production of aluminium metal (85%) and other non metal uses (10%). The remaining 5 % is used directly for specialty applications after some form of benificiation and calcination. The worldwide production of aluminium metal in 2004 amounted to 25,9 million tonnes and the production of alumina is estimated at 56,8 million tonnes. This translates to an estimated consumption of 87 million tonnes of aluminium tri-hydrate in 2004.

The total non metallurgical market of direct application of bauxite for non metallurgical uses amounted to 5,4 million tonnes in 2001. Table 18 specifies the world production of aluminium in some relevant countries in 2002. Multiplication of these figures by a factor 1.6 gives a fair idea of the amounts of metallurgical grade alumina consumed.

Country	Production 2002 (000 tonnes)
China	4 300
Russia	3 347
Canada	2 709
United States	2 707
Australia	1 836
Brazil	1 318
Norway	1 096
South Africa	676
Germany	650
India	650
Venezuela	570
France	450
Netherlands	300
Mozambique	273
Ukraine	112
Indonesia	160
Others	4 746
Total	25 900

Table 18: Primary aluminium production of selected countries in 2002

In the Netherlands the yearly production of aluminium is about 300 000 tonnes per year of which 200 000 tonnes by Pechiney Nederland in Vlissingen and 100 000 by Aluminium Delfzijl, belonging to the aluminium division of Corus Nederland.

6.3.2 Prices

Bauxite and alumina are mostly sold under long term contracts. The price details of such contracts are not made public. Spot prices for various grades of alumina and bauxite are published in trade journals. These prices are mostly indicative and sometimes published with great delay.

At the beginning of 2005, prices for various grades of bauxite and alumina were quoted by Industrial Minerals as follows:

Grade	Al_2O_3 content	Delivery mode	Price/tonne	Source
Alumina, calcined	98,5-99,5%	Delivered in UK	£ 345-440	IM
Bauxite, refractory calcined, China	>87%	FOB China	$ 135-160	IM
Bauxite, refractory, Guyana	ns.	FOB US Gulf	$ 160-170	IM
ATH (ground, non-metallurgical)	high, ns.		$400	IM
Alumina, metallurgical grade	n.s.	n.s.	$310-490	USGS

Table 19: Prices of various grades of bauxite and alumina. (ns. = not specified) (IM = Ind.Min. january 2005, USGS = USGS Mineral commodity summaries 2005)

The published price for metallurgical grade alumina in the United States varied from $310 to $490/ton.

6.4 Possible application of the sequestration product

When using anorthite as a sequestration mineral one tonne of CO_2 may theoretically produce 3,55 tonnes of aluminium tri-hydroxide, i.e. when a pure anorthite is being used. A 600 MW coal fired power plant using full sequestration would thus generate 8 to 9 million tonnes of $Al(OH)_3$.

Based on the nature of the process one might expect that aluminium hydroxide produced would be applicable in the market for aluminium trihydrate or after calcining in the market for alumina. However this would put rather stringent requirements on the composition, i.e. low contents of SiO_2 and $CaSiO_2$, components that may co-precipitate with the aluminium hydroxide.

The restricted market for non-metallurgical uses of ATH would not be able to adsorb the output of one single power plant and would be severely upset.

The market for metallurgical grades of alumina, being an order of magnitude larger than for non-metallurgical uses, could easier adsorb the sequestration product. Nevertheless, the alumina production of one power plant would already disturb the market, leading to lower prices.

7. MINERAL RESIDUE

7.1 Introduction

The use of olivine (dunite) as a sequestration mineral will result in a certain amount of unreacted material. In model calculations, Jonckbloedt (1997) comes to a residue of 36 g unreacted olivine plus inerts per 190 g of olivine in a model mass balance when dissolving olivine in sulphuric acid. This is about 19% of the input material. Even if one would succeed in dissolving all the olivine, a residue of acid resistant minerals such as chromite, sulphides, spinel, magnetite, pyroxene and amphibole, would remain that form natural components of dunite. This residue will be in the order of a least a few, say 5 wt% of the input material (see also the composition of olivine and dunite in the report by Geochem, 2005). Consequently, it is estimated that one ton of CO_2 sequestered will generate between 0,1 and 0,3 tonne of unreacted material.

7.2 Quality of the residue

7.2.1 Composition

Except for unreacted olivine the residue may be composed of:

Silicate minerals	
- pyroxene	$ABSi_2O_6$ (A=Ca,Mg,Na,Mg,Fe; B=Mg,Fe,Cr,Mn,Al)
- amphibole	$A_{2-3}B_5(Si,Al)_8O_{22}(OH)_2$ (A=Mg,Fe,Ca,Na; B=Mg,Fe,Al)
Non-silicate minerals	
- chromite	Cr_2O_3
- magnetite	Fe_3O_4
- spinel	$(Mg,Fe,Mn)Al_2O_4$
- sulphides	pyrite (FeS_2)

The normal contents of the non-silicates in the original dunite are in the order of a few tens of one percent each. Through the sequestration process the non-silicates will become concentrated in the residue to contents in the order of a few percent.
When nitric acid is used in the dissolution of the dunite at least part of the sulphides will be oxidized to sulphates and the contained iron and nickel will become part of the Mg-nitrate solution for further processing.

7.2.1 Leaching characteristics

Since the mineral residue of the sequestration process is the product of reactions with strong acids, the residue may be considered inert from an environmental point of view and will have good leaching characteristics on condition that the residue is well washed after the acid processing.

7.3 Possible application of the sequestration product

The amount of mineral residue generated by a conventional coal fired 600 MW power plant using full mineral sequestration will be in the range of 250 000 to 750 000 tonnes per year.

Considering the good leaching characteristics of the residue, its application as fill in construction projects is an evident possibility. A more attractive use of the residue could be as a secondary ore of chromium. Chromium in olivine generally occurs as small exsolved plates of chromite (Cr_2O_3) a very resistant mineral. Another possible mineral is chromium spinel ($FeCr_2O_4$). It is very likely that these minerals can be physically removed from the residue without any chemical processing.

7.4 Markets and prices

7.4.1 Fill material

The market for fill sand is virtually limitless. In the Netherlands an estimated 50 million m^3 or about 30 million tonnes of sand per year are used for filling purposes. Quality constraints are generally low and mostly concern the silt and lutum fraction of the material. As a result the price of the material is low and in the order of nil to a few Euros/m^3 ex quarry for the better qualities. Transportation costs often make up a considerable part of the value at the site of application of the sand.

7.4.2 Chromite

Assuming a chromite content of 0,2 wt% of the processed dunite, a conventional 600 MW power plant would generate about 8 000 tonnes of chromite per year. There would be no problem for the world market to adsorb such an amount. In 2003 the world mine production of chromite ore amounted to 14,9 Mt containing 4,7 Mt of chromite.

91% of the production was used for metallurgical purposes in the production of ferrochromium (stainless steel). The remainder is used for the production of refractories and chemicals. Table 20 gives an over view of the main producers of ferrochromium and their own chromite ore production. The average chromite content of the ore is estimated at 31 wt%. For the production of one tonne of ferrochromium an average 1,1 tonne of chromite is needed.

Country	**Ferrochromium**	**Chromite ore**
South Africa	2 2470	7 405
Kazakhstan	993	2 928
China	500	200
India	469	2 210
Russia	357	116
Finland	250	549
Zimbabwe	245	726
Brazil	196	391
Sweden	111	<5
Netherlands	<17	0

Table 20: Main producers of ferrochromium in the world and their chromite ore production.
(US figures are withheld to avoid disclosing company proprietary data)

From Table 21 it becomes clear that both China and Russia are importers of chromite ore.
The price of chromite has drastically increased in 2004. From 2000 to 2003 the average price ranged from 55 to 65 US$/tonne. Current prices are quoted by Industrial Minerals as follows (IM January 2005):

Grade	**Chromite content**	**Price US$/tonne**
Metallurgical	40 wt%	70-80
Chemical	46 wt%	75-125
Refractory	46 wt%	100-120
Foundry	46 wt%	120-140

Table 21: Chromite prices January 2005
(Ind. Minerals, Jan 2005)

REFERENCES

Bayer 1994, Technische daten anorganische Pigmente

Canadian Minerals Yearbook 2001, Silica by Michel Dumont

Cornell R.M., U.Schwertmann, 1996. The iron oxides; VCH Verlagsgesellschaft, Weinheim, Germany

Jonckbloedt, R.C.L., 1997: The dissolution of olivine in acid, A cost effective process for the elimination of waste acids; PhD Thesis, University of Utrecht

Geochem Research BV, 2005: An inventory of mineral resources for CO_2-sequestration; Report prepared for the Project Plan CATO.

International Iron and Steel Institute, Feb 21, 2005: Crude steel production, executive summary, January 2005, http://www.worldsteel.org

Industrial Minerals, issue April 1987: Silica, is the choice crystal clear? p25

Industrial Minerals, issue January 1996: Fused Magnesia, the blender's choice, p19

Industrial Minerals, issue January 2000: Silicon Carbide, the true grit of the market, p29

Industrial Minerals, issue February 2000: Mineral Flame retardants, Overview and future trends, p19

Industrial Minerals, issue October 2000: Full steel ahead, dead burned magnesia's market deprive, p37

Industrial Minerals, issue June 2002: Silica Flour, The finest money can buy, p46

Industrial Minerals, issue October 2002: High purity dead burned magnesia, p40

Industrial Minerals, issue January 2005: IM prices, p72.

Mining Journal, London, February 4, 2005: LME Metal stocks and prices, p.6

United States Geological Survey, Minerals Yearbook 2003: Magnesium Compounds by Deborah A. Kramer

United States Geological Survey, Minerals Yearbook 2003: Iron oxide pigments, by M.J. Potter

United States Geological Survey, Minerals Yearbook 2003: Iron ore, by J.D. Jorgenson and W.S. Kirk

United States Geological Survey, Minerals Yearbook 2002: Bauxite and Alumina, by P.A. Plunckert

United States Geological Survey, Minerals Yearbook 2002: Silica by Thomas P. Dolley

United States Geological Survey, Minerals Yearbook 2003: Chromium, by J.F. Papp

United States Geological Survey, Mineral Commodity Summaries, January 2004: Sand and Gravel by Thomas P. Dolley

United States Geological Survey, Mineral Commodity Summaries, January 2004: Quartz Crystal Industrial by Thomas P. Dolley

United States Geological Survey, Mineral Commodity Summaries, January 2004: Magnesium Compounds by Deborah A. Kramer

United States Geological Survey, Mineral Commodity Summaries, Jan 2005: Iron ore, by J.D. Jorgenson

United States Geological Survey, Mineral Commodity Summaries, Jan 2005: Bauxite and alumina, by P.A. Plunckert

United States Geological Survey, Mineral Commodity Summaries, Jan. 2005: Aluminum, by P.A. Plunckert

United States Geological Survey, Mineral Commodity Summaries, Jan 2005: Chromium, by J.F. Papp

United States Geological Survey Open File Report 01-341, Magnesium its Alloys and Compounds, Deborah A. Kramer (preliminary report)

Internet:

http://www.accuratus.com/fused.html
http://www.sciner.com/Opticsland/FS.htm
http://www.indexmundi.com/en/commodities/minerals/silica/silica_table12.html
http://www.minerals.nsw.gov.au/invest/fusedsil/text1.htm
http://minerals.er.usgs.gov/minerals/pubs/commodity/magnesium/
www.mrn.gouv.qc.ca/english/ mines/minerals/minerals-**magnesite**
http://www.ita.doc.gov/td/industry/otea/trade-detail/Latest-Month/Exports/25/251910.html
http://www.nrcan.gc.ca/mms/pdf/nfo/nfo00/mag-e.pdf