AUSTRALIA
We Norsk Hydro A.S.,
of Bygdoy alle 2,,
0257 Oslo 2,,
NORWAY.

hereby apply for the grant of a standard patent for an invention entitled:

METHOD FOR PRODUCTION OF MAGNESIUM CHLORIDE

which is described in the accompanying complete specification.

Details of basic application
Number of basic application: 872945
Convention country in which basic application was filed: NORWAY
Date of basic application: 15 July 1987

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

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PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
Norsk Hydro A.S.

By:

Our Ref : 96975
DOE Code: 1346/1346

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In support of the Convention application made by
Norsk Hydro a.s
(hereinafter called "applicant(s) for a patent") for an
invention entitled "Method for production of magnesium chloride"

I/We (c) Arne Sundnes of Norsk Hydro a.s of
Bygdoy alle 2, 0257 Oslo 2,
NORWAY.

do solemnly and sincerely declare as follows:
1. I am/We are the applicant(s).
   (or, in the case of an application by a body corporate)
2. (f) Glør Thorvald Mejdel, Hesteskoen 1, 3900 Porsgrunn, Norway
Hanne Merete Baumann, Sam Eydesgt. 18, 3900 Porsgrunn, Norway
Kjell Wallin Tveten, Ilen Terrasse 11, 3700 Skien, Norway
   is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)
is/are entitled to make the application are as follows:
   (g) Applicant is the assignee of the inventors
   (Note: Paragraphs 3 and 4 apply only to Convention applications)
3. The basic application(s) for patent or similar protection on which the application is based
   is/are identified by country, filing date, and basic applicant(s) as follows:
   (h) Norwegian patent application No. 872945 of July 15, 1987
   Norsk Hydro a.s
4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s)
made in a Convention country in respect of the invention the subject of the application.

Declared at Oslo, Norway
Dated June 6, 1988

For Norsk Hydro a.s
Arne Sundnes

To: The Commissioner of Patents

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia
such a way that a layer of lumps is situated above the fluid level. New magnesite lump is fed to the upper part of the reactor. By using large lumps foaming is prevented, and better separation of gas/fluid is achieved. A part of the perceptible heat in released CO$_2$ by the leaching process is used for preheating of lumps in the upper part of the reactor. Depending on whether more or amphotericite lump...
Method for production of magnesium chloride, for use in the production of magnesium metal, by leaching of magnesite in hydrochloric acid, wherein a two-stage leaching process is used where coarsely crushed magnesite lumps are dissolved in a first stage by introducing hydrochloric acid and where the solution leaving the first stage is led to a second stage where finely ground magnesite or hydrochloric acid is added to obtain approximately equivalence between magnesium and chlorine, and followed by a purification stage where the impurities are precipitated.
Method for production of magnesium chloride

Our Ref: 96975
POF Code: 1346/1346

The following statement is a full description of this invention, including the best method of performing it known to applicant:
The present invention concerns a method for production of magnesium chloride with sufficiently high purity for production of magnesium metal, by dissolving magnesite (MgCO₃) in hydrochloric acid and with subsequent purification of the raw solution by precipitation of undesired impurities.

Raw magnesite ore is found in many qualities according to the place of origin and with different reactivities. Macrocristalline magnesite can have crystalites greater than 5 mm, cryptocrystalline magnesite can have crystalites smaller than 0.1 mm. By leaching of MgCO₃ the grain boundaries are first attacked, in such a way that each single crystal grain is loosened. It is therefore a great difference of reactivity between cryptocrystalline and macrocrystalline material.

It is known that magnesite has been used as a basis for production of magnesium chloride. From Hans Jedlicka: "Production of Magnesia (+ 99% MgO) by the Ruthner-HCl-Route", Andritz-Ruthner Industrianlagen Aktiengesellschaft, Aichholzgasse 51-53, A-1120 Vienna, pp 5-7, it is known a method for production of magnesium oxide based on leaching of magnesite with hydrochloric acid. Magnesium, as well as iron, aluminium, chromium, manganese, calcium etc. in the raw material are dissolved by the formation of chlorides. In this process finely ground magnesite is used. The process is based on a raw material having a grain size smaller than 0.3 mm. In addition to a resource demanding and expensive grinding process, foaming problems often arise when such a finely ground material is used. Fine grains have a tendency to stick to the
surface of the bubbles and form a stable foam which makes the separation of the gas from the fluid difficult. This gives low production per volume of the reactor. According to this process possible remaining hydrochloric acid is neutralized by adding ultra-basic reactive flue-dust until a pH-value between 4 and 6 is reached. It is stated that by this pH value hydroxides of all trivalent impurities are completely precipitated. Our experience is, however, that within this pH range the precipitation of divalent heavy metals, e.g. nickel, will be insufficient.

Thus the object of the invention is to obtain a process for production of magnesium chloride with high productivity per reactor volume. It is therefore important to avoid foaming to obtain good separation of gas/fluid.

Another object of the invention is to obtain a sufficiently pure product in respect of heavy metals, e.g. nickel. It is therefore important to obtain a process with fast and efficient precipitation and separation of the impurities.

A further object of the invention is to develop a process which makes it possible to use cryptocrystalline as well as macrocrystalline magnesite. It is also an object to be able to use large lumps of magnesite and thereby reduce the crushing to a minimum.

By this invention one has developed a method where magnesium chloride can be produced, using magnesite of varying reactivity. To dissolve the magnesite a two-stage process is used. In the first stage large magnesite lumps (5-400 mm) are dissolved in a reactor where hot hydrochloric acid is fed into the bottom of the reactor, and the reaction fluid is drained out some distance below the top of the reactor, in
such a way that a layer of lumps is situated above the fluid level. New magnesite lump is fed to the upper part of the reactor. By using large lumps foaming is prevented, and better separation of gas/liquid is achieved. A part of the perceptible heat in released CO₂ by the leaching process is used for preheating of lumps in the upper part of the reactor. Depending on whether macro- or cryptocrystalline raw material is used, one will get an excess or deficit, respectively, of hydrochloric acid in the overflow to the second reaction stage. The proportion between magnesium and chlorine ions is therefore adjusted in the second reaction stage by adding either finely ground magnesite or concentrated hydrochloric acid, in such a way that equivalence, or a slight excess of acid is obtained.

In the purification process undesired impurities (phosphates and heavy metals) are removed by increasing the pH of the solution, adding an excess of lightly calcined reactive MgO or Mg(OH)₂, eventually combined with oxidation of oxidable ions with a suitable oxidation agent. It is favourable to add oxide (hydroxide) in several stages - first to neutralize free acid and thereafter to add an appropriate excess. The excess of oxide/hydroxide is so high that one should normally expect to obtain precipitation of magnesium-oxichloride. Surprisingly it was found that the formation of this is very slow and first occurs after several hours. A large excess of magnesium oxide/hydroxide is necessary to obtain satisfactory purification of the solution, and surprisingly it has a favourable effect on the time of filtration during the final separation of the impurities by filtration.

Other features of the invention are described in more detail below and are also shown in the figure, which schematically shows the manufacturing process.
Coarsely crushed (5-400 mm) lumps of magnesite are filled into the first leaching reactor 1 through a feeding mechanism 2 at the top of the reactor. Especially preferred the magnesite lumps have a size of 5-200 mm. This reactor 1 is shaped as a high, slender tower. A flow of hydrochloric acid solution with a concentration of 20-40%, preferably 28-34%, is led via a supply pipe 3, into the bottom of the first leaching reactor 1. The acid is preheated to 40-90°C.

During the dissolving of magnesite the following reaction takes place:

\[ \text{MgCO}_3 + 2 \text{HCl} = \text{MgCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \]  (1)

The reaction product is drawn off through a pipe 4 some distance (about one reactor diameter) below the top of the reactor 1 and is led via an overflow-pipe 5 to the second leaching reactor 6.

The upper part of the reactor 1 is used for separation of fluid and gas (carbon dioxide and vapour containing HCl). The relatively coarse lumps of magnesite in the reactor - especially above the fluid level - improve the separation of gas and fluid by coalescing the gas bubbles. Thus problems of foaming and droplets entrained in the waste gas are efficiently counteracted. The carbon dioxide gas which is developed by the reaction will, above the fluid level, utilize some of its heat content for preheating of the magnesite fed to the reactor. The gas is further led via a waste gas pipe 7 to an absorption tower 8 for recovering its content of hydrochloric acid vapour by absorption in water.

To avoid problematically high contents of hydrochloric acid in the gas leaving the reactor, the acid temperature and reproduction load for a given quality of magnesite is chosen in such a way that at least 85% of the supplied hydrochloric
Acid will react to magnesium chloride at this stage. By greater yields (above 85%) a considerable reduction of the vapour pressure of HCl above the solution is gained.

When the coarse pieces of magnesite are attacked by the hydrochloric acid, single crystals will normally loosen from the pieces. Depending on the size of the grains and the velocity of gas and fluid through the reactor, a greater or smaller part of the single crystals will follow the fluid flow out through the overflow pipe 5 to the second leaching reactor 6.

Also the reaction rate will be strongly dependent on the grain structure. Thus it is found that some cryptocrystalline magnesites with single crystals smaller than 0.1 mm will react up to 100 times faster than macrocrystalline magnesites with single crystals in the range 1-3 mm. Depending on the origin and the crystal structure of the magnesite the composition of the solution in the overflow line 5 will vary from strongly acidic solution with a small amount of magnesite grain contained by use of a macrocrystalline magnesite, to a nearly neutral solution with a large excess of microcrystals in the fluid when microcrystalline magnesite is used. Either acid or finely ground magnesite must therefore be added to the second leaching tank to obtain the desired composition.

If desired the temperature difference between outlet and inlet in the first leaching reactor 1 can be reduced by recirculation of the solution from the second reactor 6. This is, however, not shown in the figure.

The second leaching stage is carried out in a stirred tank reactor 6. Depending on the stoichiometric ratio between free acid and magnesite particles contained in the overflow line 5, finely milled (<3 mm, preferably <0.5 mm) magnesite is
added via a dosage equipment 9, or concentrated hydrochloric acid is added via a supply line 10.

The addition of magnesite will mainly be used when macrocrystalline magnesite with low activity is used, while addition of acid is needed when cryptocrystalline raw materials are used, as more magnesite particles are contained in the fluid leaving the first leaching tank than what is necessary to neutralize the low excess of acid.

The feed of magnesite, respectively hydrochloric acid, to the second leaching stage is adjusted in such a way that preferably more than 98% of the amounts of acid and magnesite added to the two leaching stages will react. The carbon dioxide gas released by the reaction is led via the gas line 11 to the common scrubber 8, while the fluid from the second leaching stage is led via an overflow line 12 to a first purification stage.

Raw magnesite contains several impurities (Fe, Ni, Mn, Si, Al etc.) which are also dissolved as chlorides during the leaching. To obtain a satisfactory product it is therefore necessary to precipitate the undesired contaminations from the raw solution in modifications that readily can be filtered off. Heavy metals are precipitated as hydroxide in one or two stages. In the figure the purification stages are shown consisting of one or several stirred tank reactors 13,14,15 in series with overflow lines 16,17,18 between these. Finely crushed (<0.5 mm), reactive, slightly calcined magnesium oxide or hydroxide is fed to the tanks via one or several feeders 19,20. Magnesium oxide is fed in an excess of 2–7 kg/m³ solution, preferably 3–4 kg/m³, more than needed to neutralize the content of free acid in the solution. Of process control reasons it may be favourable to add the magnesium oxide in two stages: first neutralize the free acid, and then add the desired excess.
The excess of oxide or hydroxide used will bring the pH of the solution to a value where one would expect precipitation of magnesium oxichloride. Surprisingly it is found that the formation of oxichloride is very slow and will only appear several hours after the filtration and separation of the contaminations is carried out (see below).

To ensure the best possible complete reaction and thereby utilization of the magnesium oxide, it is important that the residence time distribution for the solid substances is as narrow as possible. It is therefore favourable to divide the process into several stages of stirred tanks, of which only one or two are fed by magnesium oxide.

By the alkalinity which is obtained by the excess of magnesium oxide, the actual acid soluble heavy metal impurities will precipitate as hydroxides and eventually phosphates, if present in the raw material, and can be removed by a following filtration. To the extent an especially low content of iron in the filtrate is desirable, this can be attained by oxidation of bivalent iron ions to trivalent by adding oxidation agents (sodium hypochlorite, hydrogen peroxide etc.) to the leaching or purification stages. This is not shown in the figure.

The great excess of magnesium oxide or magnesium hydroxide is important to obtain low content of heavy metals. A typical analysis of MgCl₂-solution shows a reduction of the iron content from 400 ppm to less than 10 ppm. The content of nickel obtained is <0.5 ppm. With lower excesses of MgO, however, the nickel content will reach several ppm. Also the content of phosphorus can be reduced to <1 ppm. Although the high magnesium oxide excess in the solution should imply that the concentration is in a range where magnesium oxichloride is expected to be precipitated, this does not occur until after several hours.
The solution containing precipitated impurities in the last purification stage is leaving this via an overflow line 18 to a continuous vacuum filter 21 where the solid substances are removed for disposal. For this purpose belt filters seem to be suitable, but also other types of filters (rotating drum filters etc.) could be used. Surprisingly it has been found that a high excess of magnesium oxide (hydroxide) also acts favourably on the filterability. Lowering the excess of magnesium oxide worsens the filterability; this can mean a factor of until 10 in filtering time.

The filtrate, which will be a very clean, but alkaline magnesium chloride solution with a concentration in accordance with the strength of the hydrochloric acid used, is leaving the filter 21 via a line 22 to a stirred tank 23 where the pH of the solution is reduced to the desired value by adding hydrochloric acid through a line 24. This adjustment is also necessary to avoid precipitation of magnesium oxichloride, which otherwise, due to the excess of magnesium oxide, would precipitate by cooling and long stay.

The product of the process, the magnesium chloride solution, will leave through overflow 25 from the tank 23 for intermediate storage for later production of magnesium metal.

Example 1

In a pilot plant a first leaching reactor 1 was filled with macrocrystalline magnesite lumps (5-50 mm), 25 l/h 30% HCl at a temperature of 80°C was fed to the bottom of the reactor. The reactor was made of a pipe with a diameter of 250 mm and total height 1250 mm where the reaction fluid was drained off 900 mm above the bottom. The solution which was transferred to the second leaching reactor 6, contained 4.5% free hydrochloric acid at a temperature of 85°C. The second leaching reactor 6 had a fluid volume of 44 l and was equipped with a
stirrer. Finely ground magnesite was fed to the solution in such an amount that the solution leaving the tank contained 0.5% free HCl. The solution leaving this tank to the first purification tank contained 400 mg Fe/l, 5 mg Ni/l and 23 mg P/l. The purification stages consisted of three stirred tanks in series, each of 10 l. To the first purification tank about 100 g/h lightly calcined MgO was supplied to bring the solution up to a pH sufficiently high for precipitating trivalent iron oxide. To the second purification tank further 80 g MgO/h was added. Furthermore approximately 50 ml/h 10% H₂O₂ was added to this tank, sufficiently to oxidate all iron to trivalent. The last precipitation tank's only function was to increase the residence time and had no further inlets. The suspension was filtered on a small rotating filter, and about 400 ml/h 30% HCl was added to the filtrate to bring the pH of the solution down to about 7. The resulting solution contained 33.5% MgCl₂, while the content of impurities, as for example Fe, Ni and P was reduced to respectively <10, <1 and <0.5 mg/l.

Example 2

The same pilot plant as described in Example 1 was used. The first leaching reactor was filled with cryptocrystalline magnesite lumps (5-50 mm) and fed with 20 l/h 30% HCl at 70°C. The solution which was drained off from this reactor, was nearly neutral (<0.05% free HCl), but was white as milk because of the unreacted grains of magnesite entrained in the solution. To the second leaching reactor 6, 5 l 30% HCl was added per hour. The solution from this tank was approximately clear and contained about 0.5% free acid. The solution was further treated as in Example 1 and gave a product which contained <10 mg/l Fe and 0.5 mg/l Ni. The resulting solution contained 33.5% MgCl₂.
CLAIMS
The claims defining the invention are as follows:

1. Method for production of magnesium chloride, for use in the production of magnesium metal, by leaching of magnesite in hydrochloric acid, wherein a two-stage leaching process is used where coarsely crushed magnesite lumps are dissolved in a first stage by introducing hydrochloric acid and where the solution leaving the first stage is led to a second stage where finely ground magnesite or hydrochloric acid is added to obtain approximately equivalence between magnesium and chlorine, and followed by a purification stage where the impurities are precipitated.

2. Method according to claim 1, wherein it in the first stage is used magnesite lumps in the size of 5-400 mm, preferably 5-200 mm.

3. Method according to claim 1, wherein 20-40% hydrochloric acid with a temperature 40-95°C is used.

4. Method according to claim 3, wherein 28-34% hydrochloric acid with a temperature of 70-90°C is used.

5. Method according to claim 3, wherein a temperature and load of the acid for a given quality of magnesite is chosen so that at least 85% of the hydrochloric acid added reacts to magnesium chloride in the first stage.

6. Method according to claim 1, wherein the hydrochloric acid is fed to the bottom of a reactor countercurrent to the magnesite lumps and where the fluid is drained off about 1/2-2 reactor diameters below the top of the reactor.

7. Method according to claim 1, wherein finely ground magnesite with a grain size of 3 mm, preferably 0.5 mm, is added to the second reaction stage.
8. Method according to claim 1, wherein impurities (heavy metals, phosphates etc.) are precipitated by addition of an excess of magnesium oxide or magnesium hydroxide in one or several purification stages.

9. Method according to claim 8, wherein 2–7 kg/m³, preferably 3–4 kg/m³, magnesium oxide or an equivalent amount of magnesium hydroxide, in excess of the amount which is consumed for neutralization of the free acid is added.

10. Method according to claim 1, wherein the purified filtered MgCl₂-solution is adjusted to desired pH by adding HCl.

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PHILLIPS ORMONDE AND FITZPATRICK
Attorneys for:
NORSK HYDRO A.S.