Studies in chlorination : Part I - Magnesite

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PREPARATION of anhydrous magnesium chloride by dehydration from hydrated magnesium chloride is not straightforward after the dehydrate stage due to hydrolysis. Magnesium oxide and oxychloride contaminate the final product in uncertain amounts.

The major uses of anhydrous magnesium chloride are for extraction of magnesium metal and preparation of fluxing material used in melting, refining and casting of magnesium and magnesium-base alloys for which it should be free from magnesium oxide, oxychloride, moisture, etc.

Various methods[1–5] have been suggested, tried and patented[6–9] for preparation of anhydrous magnesium chloride from hydrated salt but none is of commercial importance due to well known difficulties.

Anhydrous magnesium chloride free from oxide and oxychloride can be prepared synthetically by:

(1) treatment of magnesium oxide (obtained from commercial sources) with chlorine in presence of a reducing agent and
(2) by the action of chlorine compounds on magnesium oxide.

The method based on chlorine compounds proves too expensive for commercial exploitation and attention was directed to the former method which is obviously simple, involving only one step.

The most favourable reducing agents are carbon and carbon monoxide. The treatment with carbon has been favoured in the studies because production of carbon monoxide involves an additional step which is not compensated by the advantages of higher heat evolution and freedom from impurities to contaminate the product (i. e. ash of carbon).

The concept of chlorinating magnesite for the preparation of anhydrous magnesium chloride is not new. At least two industrial units[9–11] are working at present (and a number of them operated during the second world war in several countries[9]) following the original I. G. technique. The present investigation for the preparation of anhydrous magnesium chloride synthetically has explored several variables to develop the know-how and demonstrate the commercial possibilities of utilising the available indigenous raw materials.

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SYNOPSIS

A systematic study on the chlorination of salem magnesite with petroleum coke as reductant has been carried out. Porous briquettes from pulverised mixture of calcined magnesite and petroleum coke were made and their properties at different drying temperatures have been studied. Briquettes of specified composition dried under predetermined conditions were chlorinated in a laboratory scale furnace. Data on the amount of chlorine injection, furnace temperature and formation of magnesium chloride are given.

The preliminary processing of raw materials, study of their characteristics, time and temperature of chlorination, amount of chlorine injected and quantity of carbon required for reduction and chlorine efficiency have been examined.

Some of the important features for the preparation of anhydrous magnesium chloride synthetically are: (a) the state or shape of the charge in the reaction zone (b) the temperature at which the reaction is to be carried and (c) the state of the product which is removed from the reaction zone.

Studies under (a) include particle size, state of aggregation and agglomeration, etc. of the solid charge. The condition decided upon (b) will lead to the solution of (c).

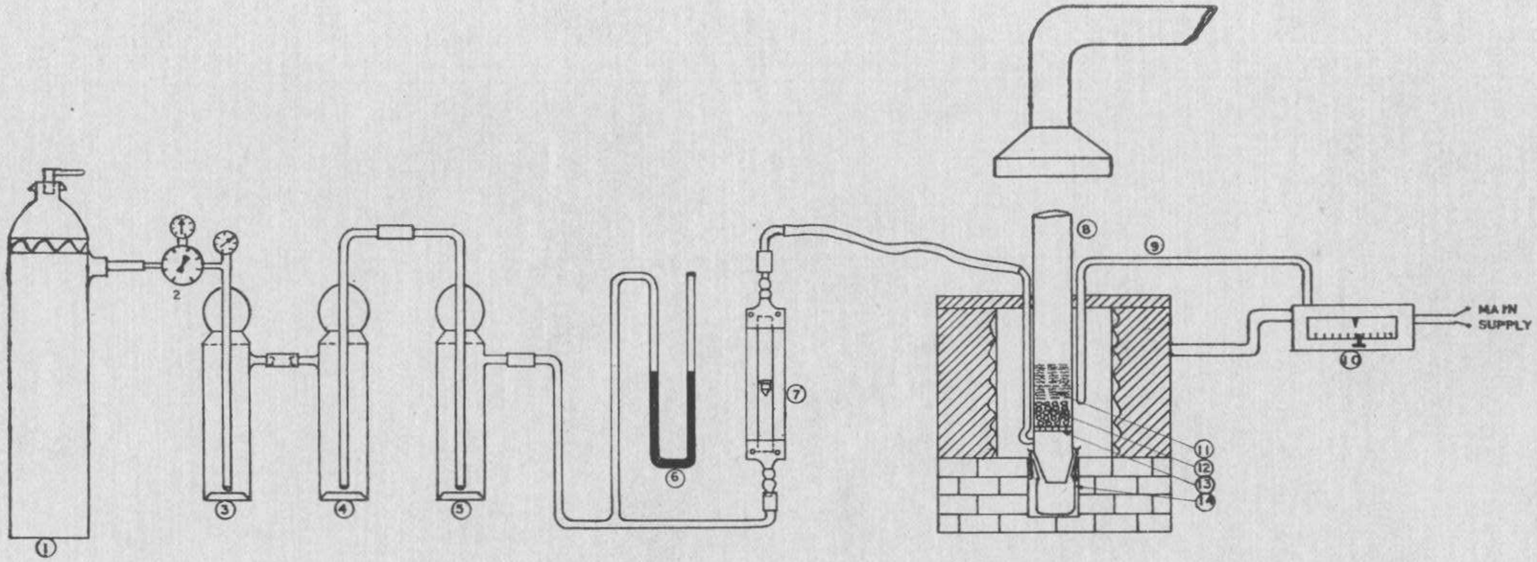
Raw materials

Salem magnesite of the following average composition has been used: MgO – 47·63% Fe_2O_3 – 0·15%; SiO_2 – 1·88%; moisture – 0·66% L.O.I. – 49·80%

Petroleum coke is of average composition: Ash – 0·83%; VM – 9·88%; moisture – 0·30%; F.C. 89·0%. magnesiumchloride solution 22°Be'.

Cylinder chlorine gas of average purity 99% +, (M/s. Alkali and Chemical Corporation of India, Calcutta) has been used.

Fig. 1 shows the apparatus used. Chlorination is effected in a 25 mm dia. quartz tube heated externally by a vertical tube furnace. The lower part of the tube is packed with graphite particles of about 5 mm dia. which supports the charge. Chlorine is injected by a side tube below the graphite bed which flows up through the graphite bed and charge in counter-current fashion.



1. CHLORINE CYLINDER
2. REGULATOR
3. GLASS WOOL FILTER
4. BLANK
5. BUBBLER
6. MANOMETER
7. FLOWMETER
8. REACTION TUBE
9. THERMOCOUPLE
10. TEMP. CONTROLLER INDICATOR
11. FEED CHARGE
12. GRAPHITE BED
13. PERFORATED GRAPHITE DISC
14. RECEPTACLE

1 *Chlorinating apparatus*

The reaction product being liquid at reaction temperature passes through the graphite bed and collects in a silica receptacle, fitted at the lower end of the quartz tube. The top is open to atmosphere under an exhaust duct. The quartz reaction tube with graphite bed is raised to the reaction temperature when the fixed quantity of briquettes or pellets is charged through the open end of the reaction tube. Chlorine injection starts simultaneously with the feeding of the charge.

Raw magnesite is calcined at 1050°C and then crushed to -60 mesh; magnesium oxide content of the calcined magnesite is 93·54%.

Petroleum coke is calcined at 700°C under nitrogen atmosphere and crushed to -60 mesh, having the following approximate analysis: ash 0·95%, VM 4·46%, moisture 2·06%, F.C. 92·53%.

Briquettes are prepared from an intimate mixture of calcined magnesite and petroleum coke in the proportion of 10 : 3 with magnesium chloride solution as binder. Cylindrical briquettes of about 12 mm dia. are pressed under various pressures.

Pellets of about 7 mm dia. are also prepared from the same composite mix in a drum pelletiser.

Both briquettes and pellets are heat-treated under standardised condition (360°C max.) to reduce the free moisture and volatiles and to make them coherent and mechanically strong.

The physical properties viz. bulk density, porosity, compressive strength, etc. of both briquettes and pellets are measured. These are then chlorinated. Results are shown in Table I.

TABLE I Effect of physical properties on chlorine efficiency

Chlorination time ... 2 hours
Temperature ... 900°C
Amount of chlorine injected ... Theoretical

Physical properties			
Bulk density g/cc.	Porosity %	Compressive strength kg/sq. cm.	Chlorine efficiency %
1·25	45·29	21·73	67·61
1·39	44·04	28·69	68·32
1·49	42·90	58·91	56·37
1·66	41·43	425·4	53·46
1·80	37·10	773·4	50·75

The effect of amount of chlorine injected on chlorine efficiency is shown in Table II. Table III shows the effect of temperature on chlorine efficiency. Table IV shows the effect of time on chlorine efficiency.

The effect of amount of carbon on chlorine efficiency is shown in Table V.

TABLE II

Chlorination time ... 2 hours
Temperature ... 900°C
Bulk density of briquettes ... 1·39 g/cc.

Amount of chlorine injected	Chlorine efficiency %
Theoretical	68·32
1·25 times theoretical	60·95
1·50 ,, ,,	57·67
2·00 ,, ,,	57·61

TABLE III

Chlorination time ... 2 hours
Bulk density of briquettes ... 1·39 g/cc
Amount of chlorine injected ... Theoretical

Temperature °C	Chlorine efficiency %
850	50·36
900	68·32
950	71·28

TABLE IV

Chlorination temperature ... 900°C
Bulk density of briquettes ... 1·39 g/cc
Amount of chlorine injected ... Theoretical

Time, hour	Chlorine efficiency %
1·0	55·43
1·5	61·49
2·0	68·32
2·5	69·03

TABLE V

Chlorination temperature ... 900°C
Time ... 2 hours
Amount of chlorine injected ... Theoretical

Excess carbon over theoretical %	Chlorine efficiency %
Theoretical	68·32
25	68·46
50	68·53
100	68·31

The optimum conditions for the briquettes with magnesium oxide-coke ratio of 10 : 3 are as follow :

Bulk density	1·39 gm/cc
Porosity	44·04%
Compressive strength	28·69 kg/sq. cm
Amount of chlorine injected	Theoretical
Chlorination temperature	900°C
Reaction time	2 hours
Maximum chlorine efficiency	68·32%

Magnesium chloride obtained analyses : MgO-0·12% $CaCl_2$-0·52%, moisture-0·13%-$MgCl_2$ 99·18%.

The pellets already prepared with magnesium oxide-coke ratio of 10 : 3 and heat-treated identically as briquettes are subjected to chlorination under the optimum conditions of briquettes. Results obtained are as follows.

Bulk density	1·23 g/cc.
Porosity	46·37%
Compressive strength	29·86 kg/sq. cm
Amount of chlorine injected	Theoretical
Chlorination temperature	900°C
Reaction time	2 hours
Maximum chlorine efficiency	75·06%

Magnesium chloride obtained analyses : MgO-0·07% $CaCl_2$-0·48% moisture 0·12%-$MgCl_2$-99·23%

Results and discussion

It is observed from Tables I to V that chlorination rate drops rapidly at higher bulk density with low porosity of the briquettes. The briquettes having bulk density of 1·25 g/cc with porosity of 45·29% are found not suitable due to their friable nature and low compressive strength. These briquettes disintegrate to powder during handling.

Increase in the amount of chlorine and carbon over theoretical requirements does not show any improvemen in chlorine efficiency. Calculation of exact carbon requirement[12] is difficult and the most satisfactory property is determined by actual chlorination tests. About 22–24% carbon in the charge material is most suitable which closely corresponds to the theoretical amount from the ratio of the mix.

With the theoretical amount of chlorine passed the chlorine efficiency is not more than 68·32%. Probably increased rate of chlorine addition with excess carbon may increase the chlorine efficiency at very high temperature. But temperature much above 950°C is not suitable due to severe attack of chlorine on the apparatus and heavy loss of product due to volatilisation.

At higher temperature the chlorine efficiency is 71·28% as shown in Table III. But there is a heavy loss of magnesium chloride formed due to volatilisation.

The maximum possible conversion of magnesium oxide to magnesium chloride is nearly completed within 2 hours. With more time the efficiency increases very little.

Chlorine efficiency has been calculated on the basis of total magnesium chloride formed which includes loss due to volatilisation and absorption in the graphite bed and the quantity of magnesium chloride collected. The loss due to volatilisation continues all along the experiment while absorption in the graphite bed starts initially with the reaction and almost ceases when the bed is saturated. The use of graphite bed is essential as a support for the solid reactants which allow the liquid magnesium chloride containing magnesium oxide in suspension or not to drain off. It also increases the reaction surface, thus increasing the reaction velocity and filtering out the solid unreactive impurities.

In all the experiments, only 12 mm high graphite lumps bed is used, which is not very effective as seen from the product analysis. The product is contaminated with adsorbed carbon and is light darkish in colour. An increase in the lump bed height to 25–30 mm should have been beneficial to remove the traces of oxide and carbon.

From the optimum results of briquettes and pellets it is found that chlorine efficiency is better with pellets as feed charge than with briquettes.

Conclusion

To achieve reasonably efficient chlorination of magnesia-carbon mix, factors such as physical nature and characteristics of briquettes and pellets, reaction time, temperature and amount of chlorine, are very important. The briquettes and pellets should not break easily during handling or disintegrate to powder inside the chlorination chamber and they must be porous enough to permit gas-solid reaction to proceed effectively.

On the basis of the observed optimum conditions, a proposal has been put forward to design a production unit with a capacity of 25 kg/day. The proposed unit should be internally heated.

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Discussions

Dr **P. K. Jena** (Banaras Hindu Uuiversity, Varanasi) : Have the authors studied the effect of bed height on the efficiency of chlorine utilisation ? It is very likely that efficiency will improve on increasing the bed height of MgO and C pellets.

It is also suggested that coked Indian lignite may result in an increased rate of chlorination.

Authors : 12 mm high beds of graphite lumps have been used and found not very effective. Bed height of MgO+C pellets has not been studied but height is not likely to improve the chlorine efficiency. Coked Indian lignite cannot substitute the petroleum coke particularly for its high impurities. The net effect will be a drop in efficiency and the need for frequent cleaning of the apparatus. We thank Dr Jena for his helpful suggestion. We will certainly look into the points he has raised, in the course of our further studies.