

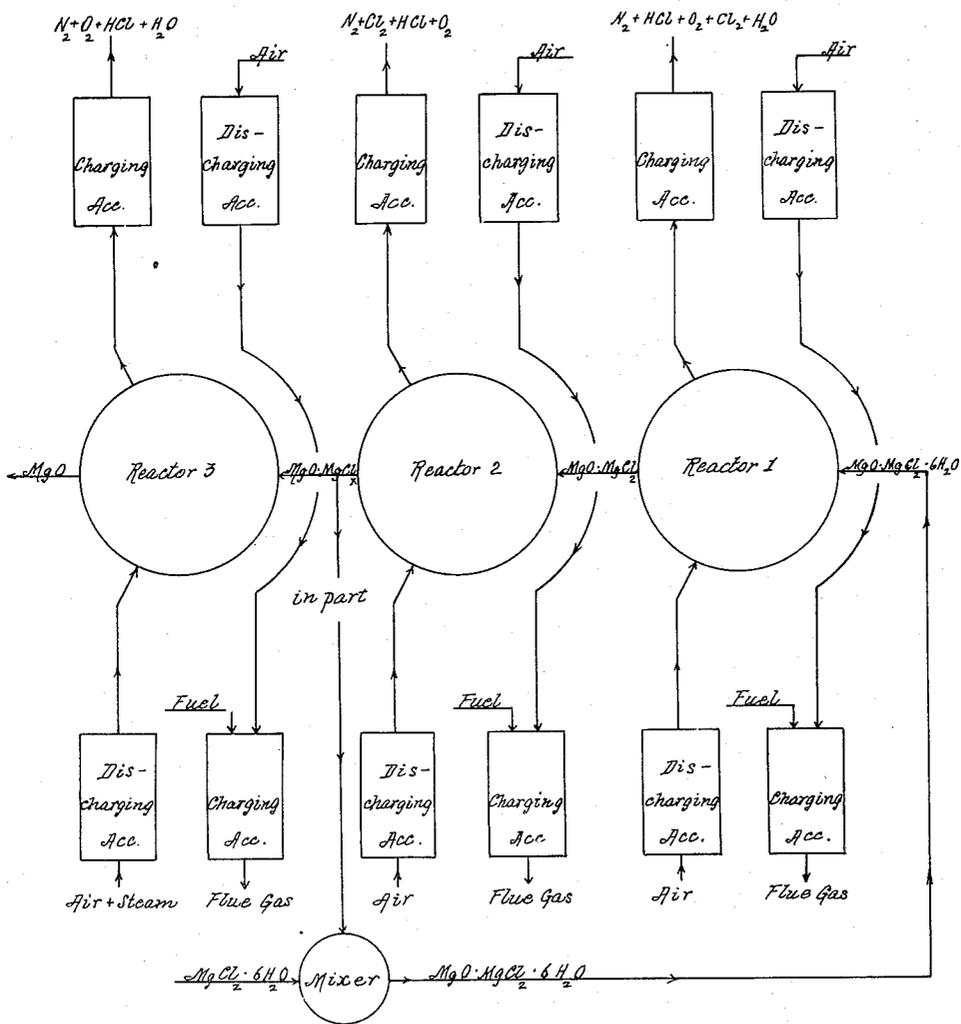
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METHOD OF PROCESSING MAGNESIUM CHLORIDES

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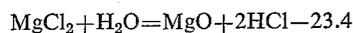
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5 Claims. (Cl. 23—201)

The chemistry involved in the decomposition of mag-
nesium chlorides by means of heat, in the presence of
oxygen and/or steam, is admittedly very old. Apparent-
ly it was known before 1850, and during the following
three or four decades it was spasmodically in use on a
limited scale. However, no success attended these trials
and it was finally abandoned everywhere. The reason for
such abandonment must be found in the technical diffi-
culties involved, so, the instant application is concerned
not with improvements in the chemistry involved but
with the mechanics of the operation.

The chemical reactions may be represented as follows:

$$\text{MgCl}_2 + \text{O} = \text{MgO} + \text{Cl}_2 - 9.6 \text{ Cal.}, \text{ and}$$



Calories. While both these reactions are endothermic
it is obvious that the input of energy is quite small.
Economic reasons are also involved in suggesting that this
ancient chapter be revived. There is in the Great Salt
Lake, Utah, an inexhaustible source of magnesium chlo-
ride. In a co-pending application, to wit, Ser. No. 791-
018, filed Feb. 4, 1959, called "Method of Making Mag-
nesium from Salt Lake Brines," I have already called
attention to this resource. Another factor is the tre-
mendous modern demand for a high-grade magnesium
oxide.

Perhaps an even more potent reason for such revival
of interest lies in the commercial chlorine-hydrochloric
acid industry. Once safely entrenched behind the enor-
mous caustic soda demand the electrolytic soda industry
now faces a complete reversal. In the electrolysis of
salt, chlorine is far the more important and caustic soda
disposal presents a real problem. It is, therefore, of
supreme importance to seek means of producing chlorine
with a substitute for caustic soda as an additional prod-
uct. Such a substitute obviously resides in magnesia
with a present market of nearly a million tons per annum.

The equations given previously as the reactions where-
by such chlorine and/or hydrochloric acid may be pro-
duced show only the anhydrous salt. Unfortunately, the
natural salt is not anhydrous but crystallizes with six
molecules of water of crystallization. Of this water, five
moles may be removed with but little loss of chlorine but
to remove the last mole by heat alone results in a copious
evolution of HCl and the formation of the oxy-chloride.
To avoid this has been a challenge for many years. In
the previously mentioned application I have added an
equally old way, namely, a prior crystallization of the
double salt with ammonium chloride, which may be de-
hydrated without loss. On subsequent heating ammonium
chloride is evolved, condensed, and re-cycled, after which
the magnesium chloride may be fused with impunity.
Another way would be to de-hydrate in an atmosphere
of hydrochloric acid, but that is rather hard to contem-
plate in any commercial operation. But as already men-
tioned, the commercial production, from the oxy-chloride,
has been operated for years though subsequently it had

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to bow to the superiority of electrolysis. I have illus-
trated my version of how that may, once more, become
of commercial merit in the drawing which I will now
describe. Subsequently I shall add a few words as to
its applicability to the anhydrous salt as well.

In said drawing, I commence at the bottom, where in
a "mixer" I commingle crystallized magnesium chloride,
which melts in its water of crystallization, with an inter-
mediate form of magnesium oxide, still retaining a little
chlorine as designated by the "x" placed beneath the
Cl. I use enough of the oxide to produce a solid mass
when the reaction is complete. Provisionally, that means
somewhat more than an equal amount of magnesium as
oxide to that present as chloride, yet rather less than
1½ times as much. In effect this mixture is similar to
the Sorel cement used in magnesia flooring. This solid
material is crushed and classified. An acceptable size is
between 15 microns and 100 microns, the dust being sep-
arated by air floating and re-cycled to the mixer.

The accepted fraction is now fed continually into the
device called "Reactor 1," containing an ordinary fluidized
bed of de-hydrated magnesium oxy-chloride. It is main-
tained in said fluidized state by the upward traverse of air
heated to about 550° C. in a discharging heat accumulator
placed in the drawing below, left, of said reactor. When
the temperature of the air drops to about 450° C. re-
versal of flow takes place and the "charging accumulator"
which has meanwhile been heating, it substituted. Above
the reactor I have indicated another pair of heat accu-
mulators that function as coolers for the gas leaving
said reactor and as preheaters for the combustion air re-
quired by the fuel. In this manner, virtually all sensible
heat can be re-cycled, only that heat being required in
effecting a chemical change being required. It will be
obvious that by thus recovering the larger part of the
sensible heat in the gas leaving the reactor and trans-
ferring it to the air of combustion I have achieved a
great economy in heat usage. It will be equally obvious
that the addition of a small continuous flow of "wet"
oxy-chloride cannot adversely effect the mechanical con-
dition of the de-hydrated, infusible material composing
the fluidized bed.

A "unit" of my system is thus seen to consist of the
reactor, which functions continuously in one direction,
and four heat accumulators that function, alternately, as
receiving and as giving out this stored heat energy. Of
course, this is a schematic representation for the sake
of simplicity. Inasmuch as it is a copy of the blast
furnace stoves of the high iron furnace it is a well known
heating technique which I have applied to a new purpose
and made regenerative as well. An actual installation
would have three accumulators both above and below
the represented reactor. Each side would then show two
accumulators discharging and one receiving heat. On
reversal of flow, the cooler one of the discharging "stoves"
would be switched to the heating cycle, and the one just
heated to its maximum temperature would be used to re-
place it. In this manner a smooth, uninterrupted flow
of hot air would traverse the fluidized bed.

In this manner the magnesium chloride is converted
to an oxy-chloride and approximately one-half of the
chlorine is evolved as hydrochloric acid together with
almost all the water of hydration. Nitrogen, unused
oxygen, steam and HCl is then represented as the gases
leaving reactor 1. I have then shown the increase in
bulk of said fluidized bed passing on to reactor 2, where
the identical operation is repeated, only, as the offending
water has been removed, the passage of hot air now
yields chlorine in place of hydrochloric acid. In a con-
tinuous process, with rather large storage in the fluidized
beds, it is impossible to make this cut absolute. A little

chlorine will be evolved in reactor 1, and a little HCl will be evolved in reactor 2, as I have indicated. The surplus increment from reactor 2 is then passed on to reactor 3 for final removal of all chlorine. This is effected by the deliberate addition of steam to the traversing air so the gas leaving the reactor again contains its chlorine as HCl, not as "free" chlorine.

Such use of steam is mandatory if it be desired to have all chlorine removed without the otherwise unavoidable rise in temperature needed if steam be omitted. The total chlorine of the feed is thus obtained in the following ratio, chlorine 40%, hydrochloric acid 60%. An excellent grade of magnesia is likewise produced if this technique be followed. Collectively, these items are most important. Unless ALL be taken into consideration as objectives of relatively equal importance my application of this old chemistry, in spite of the modern technique and the heat recuperative features, would still remain economically unremunerative.

Throughout all reactors the temperature will be maintained substantially within the range previously specified, to wit, between a low of 450° C. and a high of 550° C. Of course, any deviation from these temperatures is not fatal but within these brackets the reactions proceed smoothly. Similarly, the best place to observe such temperature is by placing the pyrometer within the space occupied by the fluidized bed. It is within this bed, where the reaction occurs, that temperature control is vital.

It will be obvious that if anhydrous magnesium chloride be substituted for the "Sorel Cement" then this three-step process becomes automatically a two-step process. The only purpose served by Reactor 1 is dehydration with consequent evolution of hydrochloric acid. If a start be made with anhydrous material then reactors 2 and 3 will suffice, and chlorine will be obtained at once. However, the second step with steam is still mandatory to produce an acceptable magnesia product. In this case the ratio of chlorine to hydrochloric acid will be about 10 to 1, by volume.

Many minor modifications suggest themselves once the plan of my operation is understood. Thus, once the fluidized bed is established in reactor 1, it will be plain that no additional water would be introduced if a liquid feed of magnesium chloride were introduced directly as an atomized product. Inasmuch as said hydrated salt melts in its water of crystallization. It is immaterial whether such an atomized spray be directed upon the surface of the bed or simply injected into the space above said bed which would then act as a spray drier, dehydration being completed in the fluidized bed into which such a spray, or rather the solids from said spray, would ultimately arrive.

However, the very reverse of this procedure would work to better advantage. Again, taking advantage of the properties of magnesium chloride, we find that three-fourths of the resident water can be evaporated with a loss of as little as 5% of the resident chlorine which will, of course, be lost as HCl. It would, therefore, be advantageous to partially dry this crystallized salt down to a water content of approximately 20%, grind it to powder, and then introduce it in this form into the fluidized bed of reactor 1. In this manner much water would be prevented from entering into the gaseous materials leaving said reactor which, in turn, would facilitate further work in the recovery of hydrochloric acid therein. The same objective would be reached if the operation in reactor 1 were two-stage instead of single stage. Let, therefore, this work be performed with a spray of fused salt in the first of these reactors, followed by a complete de-hydration in the second. Obviously, the acid from the first step would only be fit to discard while the acid from the second step would be correspondingly improved. As a final refinement fire gas might be used directly in the first stage.

Inasmuch as the decomposition of magnesium chloride is a function of time as well as temperature it is obvious that the time of residence within said fluidized bed is also a matter of importance. This must be obtained by analysis of the fraction withdrawn from said bed, but once established it is governed solely by the rate of feed into said bed. Parenthetically it may be stated that in a two-stage dehydration, as previously described it would be advisable to lower the temperature of the first stage to 300° C., or even less, and thus minimize the loss of hydrochloric acid in said stage. Having thus fully described my process,

I claim:

1. The method of processing anhydrous magnesium chloride which comprises; adding said magnesium chloride in powdered form to a fluidized bed consisting essentially of magnesium oxide with some retained chloride, maintained in a fluidized state by the upward traverse through same of air heated to a temperature between an approximate 450° C. and an approximate 550° C. with attendant evolution of chlorine gas; withdrawing continuously an amount of said fluidized magnesium oxide corresponding to the added magnesium chloride and adding said withdrawal to a fluidized bed consisting essentially of chlorine-free magnesium oxide maintained in said fluidized state by the upward traverse through same of a current of air and steam heated to a temperature between an approximate 450° C. and an approximate 550° C., thus obtaining substantially pure magnesium oxide with attendant evolution of hydrochloric acid gas; and withdrawing continuously from said fluidized bed of magnesium oxide an amount of said magnesium oxide corresponding to the anhydrous magnesium chloride originally added to the first fluidized bed.

2. The method of processing magnesium chloride which comprises; adding magnesium chloride in hydrated form to a fluidized bed of relatively anhydrous magnesium oxychloride maintained in a fluidized state by the upward traverse through same of a current of air heated to a temperature between an approximate 450° C. and an approximate 550° C. thus converting the additive hydrated magnesium chloride into substantially anhydrous oxychloride with attendant evolution of hydrochloric acid gas; withdrawing an amount of said oxychloride corresponding to the added magnesium chloride, continuously, and adding said withdrawal to another fluidized bed consisting essentially of magnesium oxide with some residual oxychloride, maintained in a fluidized state by the upward traverse through same of a current of air heated to a temperature between an approximate 450° C. and an approximate 550° C. thus converting the added oxychloride into a product consisting essentially of magnesium oxide, still retaining oxychloride, with attendant evolution of free chlorine gas; withdrawing continuously an amount of said magnesium oxide corresponding to the added oxychloride of magnesium and adding said withdrawal to a fluidized bed of magnesium oxide maintained in said fluidized state by the upward traverse through same of a current of air and steam heated to a temperature between an approximate 450° C. and an approximate 550° C. thus obtaining substantially pure magnesium oxide with attendant evolution of hydrochloric acid gas; and withdrawing continuously from said fluidized bed of magnesium oxide an amount of said magnesium oxide corresponding to the hydrated magnesium chloride originally added to the first fluidized bed.

3. The method of processing magnesium chloride set forth in claim 2, with the added step that the dehydration of magnesium chloride described therein be conducted in two steps with two fluidized beds, separate and distinct from one another, the temperature of the first bed being maintained substantially 200° C. lower in temperature than the second bed, thus performing a partial dehydration with low evolution of hydrochloric acid before transferring to the finishing bed in which the temperature

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is maintained at between 450° C. and 550° C. as previously specified.

4. The method of processing magnesium chloride set forth in claim 2, with the added step that the gaseous fluid emanating from the fluidized beds be cooled by passage through a heat accumulator; conveying the heat thus stored, on reversal of flow, to the air of combustion required in heating another heat accumulator, the second accumulator, in turn, conveying its stored heat to the fluidizing medium on reversal of flow.

5. The method of processing magnesium chloride set forth in claim 1, with the added step that the gaseous

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fluid emanating from the fluidized beds be cooled by passage through a heat accumulator; conveying the heat thus stored, on reversal of flow, to the air of combustion required in heating another heat accumulator, the second accumulator, in turn, conveying its stored heat to the fluidizing medium on reversal of flow.

References Cited in the file of this patent

UNITED STATES PATENTS

10	2,155,119	Ebner -----	Apr. 18, 1939
	2,413,292	Christensen -----	Dec. 31, 1946
	2,694,620	Lathe -----	Nov. 16, 1954