E. A. ASHCROFT.

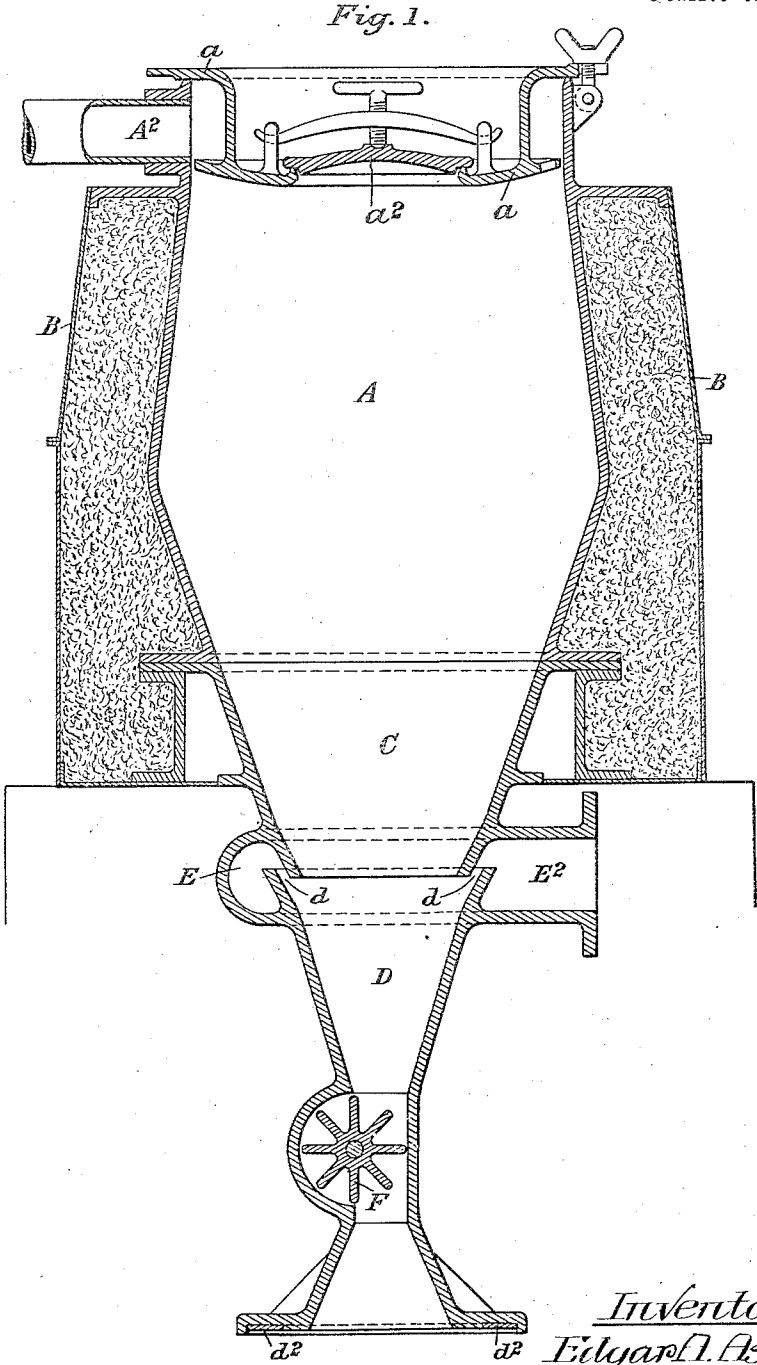
PROCESS FOR THE PRODUCTION OF ANHYDROUS MAGNESIUM CHLORID OR ANHYDROUS DOUBLE CHLORIDS OF MAGNESIUM.

APPLICATION FILED AUG. 12, 1919. RENEWED OCT. 9, 1920

1,359,652. **Patented Nov. 23, 1920.**

3 SHEETS—SHEET 1.

Fig. 1.



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by his Attorneys.
Howson and Howson

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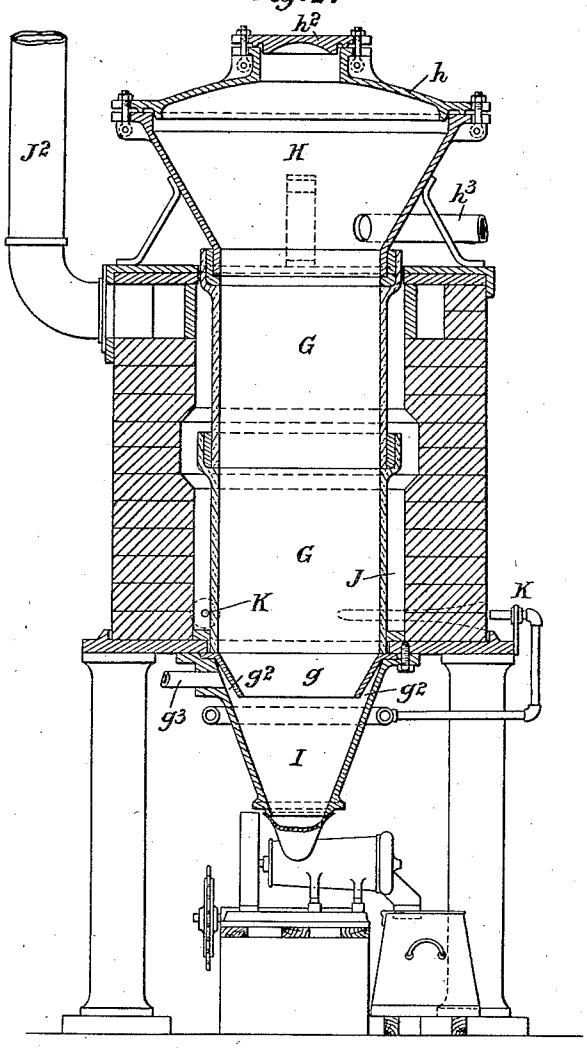
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3 SHEETS—SHEET 2.

Fig. 2.



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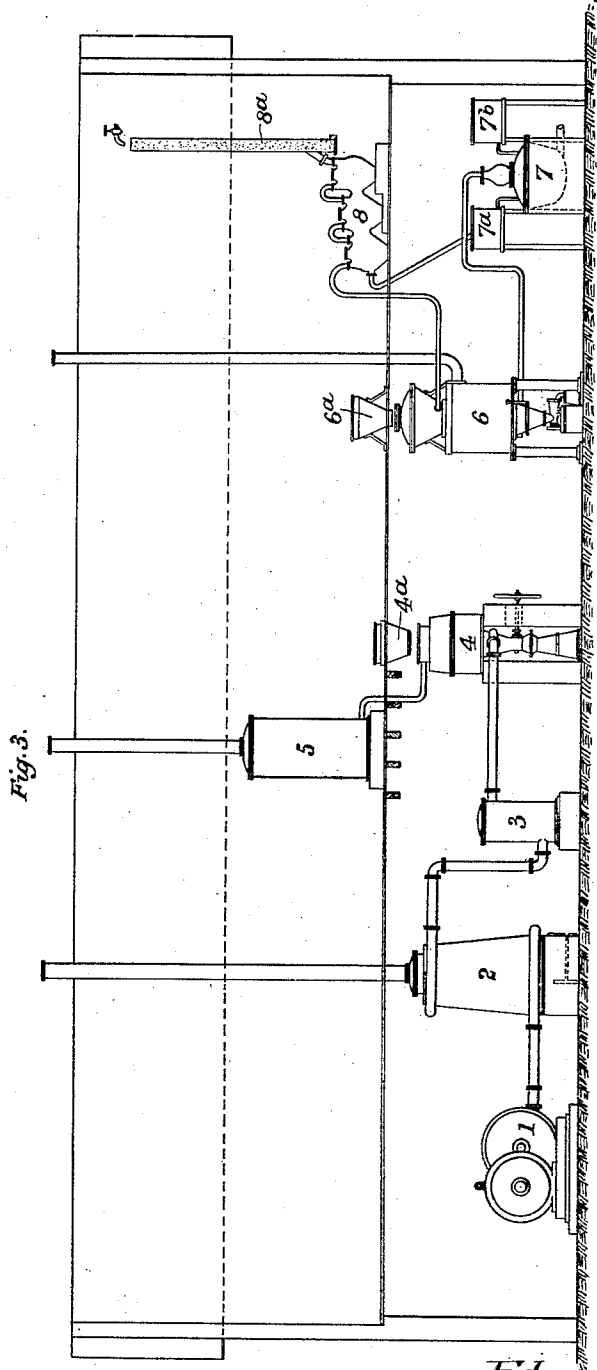


Fig. 3.

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UNITED STATES PATENT OFFICE.

EDGAR ARTHUR ASHCROFT, OF LONDON, ENGLAND.

PROCESS FOR THE PRODUCTION OF ANHYDROUS MAGNESIUM CHLORID OR ANHYDROUS DOUBLE CHLORIDS OF MAGNESIUM.

1,359,652. Specification of Letters Patent. Patented Nov. 23, 1920.

Application filed August 12, 1919, Serial No. 317,082. Renewed October 9, 1920. Serial No. 415,951.

To all whom it may concern:

Be it known that I, EDGAR ARTHUR ASHCROFT, a subject of the King of Great Britain, residing at 65 London Wall, in the city of London, England, have invented new and useful Improved Processes for the Production of Anhydrous Magnesium Chlorid, or Anhydrous Double Chlorids of Magnesium, of which the following is a specification.

My invention relates principally to the production of anhydrous magnesium chlorid more especially from the ordinary hydrated magnesium chlorid of commerce, which salt crystallizes from its solutions containing six molecular proportions of water of hydration. It is well known that the removal of water of hydration by ordinary heat processes is attended by serious difficulties and that dehydration cannot be effected by any known process, available for commercial purposes, the processes hitherto employed having been attended by serious decomposition of the neutral salt, loss of acid, and formation of basic residues.

From A. D. 1870 to A. D. 1890, or thereabout, many attempts were made to dehydrate, or "dry", hydrated magnesium chlorid (for instance by Pechiney, Weldon, Solvay and others) more particularly with a view to providing processes for the production of chlorin from the magnesium chlorid of the Stassfurt deposits. In those processes it has, at various times, been suggested to use currents of air (hot, or cold), or of other gases including hydrochloric acid gas, the latter having been suggested for the purpose of improving the equilibrium conditions according to the well known laws of mass reactions and it has also been proposed to raise the temperature of the salt progressively during treatment to avoid fusion and therefore I do not claim these operations to be novel separately considered, although I make use of them in the process according to my present invention.

In spite of the aforesaid attempts and the considerable amount of work done at about the period mentioned and having the said object in view, it is evident that none of them were complete, or successful, from a practical point of view, because, throughout the last thirty years, or so, it is well known that the whole of the anhydrous magnesium chlorid of commerce has been produced by the more elaborate and costly method of fusing the hydrated salt with ammonium chlorid (a most expensive and troublesome operation), and in more recent years by the treatment, with chlorin gas, of a fused bath of the initial compound in a converter.

I have invented novel means whereby the water of hydration can be entirely removed from hydrated magnesium chlorid without difficulty, and at but small cost. According to my invention I employ the magnesium chlorid in a suitable form as hereafter explained (preferably as needle crystals) and after removing sufficient of the water of hydration by means of a voluminous current of heated air, which raises the fusion point of the salt to above 250° centigrade, I treat the partically dehydrated crystals with a slow current of hydrochloric acid gas which need only be used in sufficient quantity to combine with the water liberated from the crystals, forming a strong solution thereof which is afterward completely recovered. During the said treatment with hydrochloric acid gas the vessel or retort, in which the treatment takes place should be externally heated, and the temperature should be slowly raised from a minimum of 150° centigrade, or thereabout, to a maximum of 650° centigrade, or thereabout, so that fusion does not take place at any period of the treatment, but incipient fusion is produced toward the end of the said treatment and the material leaving the apparatus then assumes a partially crystalline form and consists of magnesium chlorid of a very high degree of purity, 98 to 99 per cent. magnesium chlorid being possible if care be exercised in the operation.

During the preliminary drying with a voluminous current of heated air the whole of the heat is most conveniently imparted to the charge by heating the air employed, as this will prevent the fusion of the charge which otherwise would take place too readily. When from three to four molecular proportions of water, out of the total content of six molecular proportions, have been removed from the salt the melting point will be raised from about 80° centigrade, or thereabout, to about 250° centigrade, or thereabout, while no decomposi-

tion of the salt, and therefore no loss of the chlorin content, will have taken place. If, however, the dehydration by means of air be pushed much further partial decomposition will ensue with evolution of hydrochloric acid gas.

Therefore, at this stage, a slow current of hydrochloric acid gas is substituted for the air current, and thereafter the temperature is steadily raised as the water is removed from the charge.

I have found that the action of the hydrochloric acid gas under these circumstances is not merely an improvement of the equilibrium condition, but is that of a powerful desiccator, and this to such an extent that very shortly after the application of the hydrochloric acid gas to the charge, and at a temperature very little above 250° centigrade, the greater part of the water of hydration has been completely removed and carried over into the condensing apparatus in the form of a strong solution of hydrochloric acid. This solution condenses, containing about 20 per cent. hydrochloric acid. Thereafter, on continuing the same current of hydrochloric acid gas, while the charge is slowly raised to the maximum temperature of 650° centigrade, the remainder of the water is carried over from the charge and, together with it, an excess of dry hydrochloric acid gas, which, as hereinafter explained, is immediately absorbed in the water and partially saturated solution passing through the absorbing apparatus.

By this means the whole of the hydrochloric acid gas employed in this treatment is recovered in the form of a strong solution containing say 33 per cent. of hydrochloric acid, and can be used again and again for the treatment of subsequent charges by expelling the gas by means of concentrated sulfuric acid, which also can be used again and again by reconcentrating the said sulfuric acid.

By this means it is found necessary to employ only a quantity of acid nearly equivalent to the weight of the salt under treatment, such acid, as hereinbefore stated, being completely recovered and available for use again after reconcentration, and therefore the whole operation, as regards the consumption of materials, or of heat energy, is exceedingly economical.

Consequently I carry out my improved process in two stages, the first stage consisting in partial drying with a voluminous current of air, and the second stage consisting in complete desiccation by means of a slow current of hydrochloric acid gas.

Both of these operations can be carried out in batches, the apparatus being emptied and refilled after each treatment, but it is preferable to carry them out in vertical retorts, the discharge of which is continuous, and the charging of which may be intermittent as hereinafter explained.

In the first stage, consisting in the use of a very voluminous current of heated air, all the heat is imparted to the charge under treatment by the air and is absorbed completely by the charge. By a voluminous current of heated air I mean one say exceeding 50,000 cubic feet per hour per ton of charge, although it may be very much greater, say as much as 500,000 cubic feet. This stage is preferably carried on until such an amount (usually one third, or thereabout) of the total water has been removed from the initial material, so that the melting point is raised to say 250° centigrade, or thereabout, no loss of chlorin from the salt ocurring. It may however (if preferred for any reason) be carried further, some hydrochloric acid then being given off and some magnesium oxid, or oxychlorid, remaining in the charge. In such case the subsequent treatment with hydrochloric acid will correct this effect and restore the neutrality of the salt, but with a corresponding consumption of hydrochloric acid gas.

In the second stage of the process, treatment with a small, or slow, current of hydrochloric acid gas is substituted for treatment with heated air (in the same, or another vessel) and heat is applied to the charge, allowing sufficient time for the small, or slow, current of hydrochloric acid gas to remove the remaining water without decomposition of the salt, the temperature being slowly raised to say 650° centigrade.

By this treatment a product having 98 per cent., or more, of pure anhydrous magnesium chlorid can be readily obtained. The product is white and porous and remains in that condition if the temperature does not exceed, say 500° centigrade, but, as it is steadily raised to about 650° centigrade, the product becomes of a partially crystalline texture and it is completely fusible at from about 650° to about 700° centigrade. If the treatment has been carefully carried out, there will be but little, if any, magnesium oxid therein.

When the first and second stages have been successfully carried out the total loss of weight, on fusion of the finished product in a silica crucible, will not exceed one, or two, per cent. and the assay value of anhydrous magnesium chlorid will be slightly raised and not lowered by such fusion, showing that very little, or no, water remains after the second stage, but probably there will be a little occluded carbonic acid gas and other gases.

The aforesaid fusing of the product is not however necessary in practice and the product from the second stage of my process may be employed directly for any required purpose for which it is suitable; for instance,

it is found to be eminently suitable for the electrolytic manufacture of magnesium metal, or alloys.

The following example is the best way with which I am acquainted of carrying out my invention in practice, but I do not limit myself to the precise details of this particular example.

Stage 1.—The magnesium chlorid is prepared in the form of needle crystals, which can conveniently be done by allowing a solution, concentrated to a strength of about 80° Twaddell (1.400 specific gravity), to cool, from say 50° centigrade to atmospheric temperature, when more than half of the magnesium chlorid content will crystallize out and the crystals may be centrifugaled, or drained, in any suitable manner, and then be placed in the air drying apparatus and subjected to the aforesaid voluminous current of dry air at a temperature which must be lower than the fusion point of the initial hydrated charge, to commence with; for instance, in the case where the heated air is passed in an upward direction in contact with a descending charge, the air may be admitted at about 150° centigrade, and it will cool as it ascends until the incoming charge is met by air at a temperature low enough to prevent its fusion, but the air may, as the charge dries, be rather more strongly heated, say up to 250° centigrade, the object of these regulations being in any case that the crystals shall not be caused to fuse at any stage of the treatment but shall retain their form and dimensions notwithstanding the great loss of weight.

The aforesaid conditions are automatically brought about if an apparatus having a continuous discharge, as hereinafter described and illustrated, be employed, because, in that case, the cooler air near the exit therefor from the apparatus will partially dry the descending charge, which, in its turn, will be subjected to the hotter air at the lower part of the apparatus. In such an apparatus it is convenient to heat the air to a higher degree, say up to 300° centigrade.

In the accompanying drawings—

Figure 1 represents in vertical section, an apparatus suitable for use in carrying out the first stage of the process;

Fig. 2 shows in vertical section an apparatus suitable for use in carrying out the second stage of the process; and

Fig. 3 is a more or less diagrammatic elevation of a complete installation for carrying out the process.

The apparatus shown in Fig. 1 comprises a vertical retort A, of iron, or other suitable metal, which may be enameled inside and is so set as to be capable of retaining the heat which is imparted to the charge by means of the heated air. This is shown as being done by surrounding the retort by a casing B, containing a non-conductor of heat such as slag-wool.

The current of air is preferably introduced at the lower end of the retort and, in the drawing, this is shown as being effected by forming the outlet in two parts C, and D, the part C dipping somewhat into the part D, with a gap d between, this gap being surrounded by an air channel E into which heated air is passed by the inlet E^2 from any suitable source. The air passes up through the descending charge and escapes at A^2, while the treated material descends into any suitable receptacle, such as a churn, whose upper edge may fit against a resilient ring at d^2 forming an air-tight joint. F is a ribbed, or star, discharging wheel, the speed of rotation of which can be regulated, by any convenient means between say one and sixteen revolutions per minute. During the air treatment it is convenient to desiccate the ingoing air, as, by this means, a somewhat better result is obtained. Desiccation of the air however is not essential. I have shown, at the upper end of the retort A, a large cover a, for cleaning purposes and a smaller cover a^2 for charging purposes, both of which can be sealed air-tightly. The retort may also be charged continuously, but I prefer to introduce the charge intermittently, periodically removing the small door a^2, for that purpose, as the level of the material in the retort falls.

Instead of the aforesaid apparatus I may employ a similar apparatus which is charged and discharged in batches, a grating being provided underneath for distributing the air and there being suitable doors for an inlet and outlet of the material.

The operation at this stage of the treatment need only be of a few hours duration and, in the case of the continually discharged apparatus, is regulated by the rate of discharge, the temperature of the ingoing air in that case being kept constant.

It is found that, if the air treatment be carried too far, first an evolution of hydrochloric acid gas takes place due to the decomposition of the salt at the high temperature necessary for expelling the bulk of the water of hydration, and finally, when the salt is nearly dry and the temperature has reached 200° to 250° centigrade an evolution of chlorin will take place. It is neither necessary, nor desirable, to carry the treatment so far.

I therefor now proceed to the second stage of the process:

Stage 2.—This may be carried out in the same apparatus as that in which the first stage of the process is carried out, or in another vessel, or retort, which may be similar to it with the difference that means are provided for heating the charge to a temperature of 650° centigrade, or thereabout.

When the operation is carried out in the same vessel, or retort, flues are preferably provided around it for the purpose of this heating and, immediately after the treatment, according to the first stage, with a voluminous and rapid current of air, treatment by a slow current of dry hydrochloric acid gas is substituted for the air treatment, and heat is applied so as to slowly raise the temperature to 650° centigrade, or thereabout. As the hydrochloric acid gas has a strong affinity for water it will rapidly absorb the water of the charge while not causing any decomposition of the magnesium chlorid and, on leaving the hot vessel, or retort, the moisture at once condenses and can be collected in the condition of a strong solution of hydrochloric acid from which the gas can, by any known, or suitable, means, be again discharged for reintroduction to the cycle. The acid gases will not attack the metal of the vessels at the lower working temperatures of the process, but I prefer to use silica retorts for all parts with which the acid gases come in contact at a temperature exceeding 400° centigrade.

I prefer for this second stage to employ a separate apparatus and to arrange it that the material continuously discharged from the apparatus of the first stage of the treatment is intermittently introduced into the apparatus for the second stage of the treatment and then is continuously discharged from the last named apparatus.

Fig. 2 of the accompanying drawing shows in vertical section a suitable apparatus which I have devised for this purpose. The retort is shown as consisting of a body-part G, made in two sections, and an upper part consisting of a closed hopper H, with a large cover h for cleaning purposes and a small cover h^2 for charging and also an outlet I furnished with a discharge screw not shown into which outlet a depending part g projects and leaves a space at g^2 into which hydrochloric acid gas passes by the pipe g^3 and thence passes up through the descending charge and (accompanied by water vapor), away at h^3, to any suitable place of discharge. The body-part G, depending part g, and hopper and discharge parts (H and I) may be made of any suitable material. For instance the body-part and depending part may be made of silica-glass and the hopper and discharge parts may be made of iron, enameled internally. The heating of the retort is shown as being effected by a furnace J, surrounding the body-part G, and heated by gas and air admitted at any suitable points, such as are shown for instance at K, the products of combustion passing off by the chimney J^2.

This treatment with the hydrochloric gas may continue for say three, or four, hours, during which time the vaporized solution of hydrochloric acid will distil over at h^3, and can, after condensation, drip through a sight-tube into a vessel provided for its retention, surplus hydrochloric acid gas being simultaneously absorbed in water in the absorber. The hydrochloric acid absorber may consist of a series of Woulfe's bottles, or jars, terminating in a tower of small diameter packed with any suitable packing and supplied with water. By means of the sight-drip, and of a graduated vessel provided for receiving the acid, the progress throughout the period of the treatment can be accurately observed which is very convenient in practice.

After the aforesaid treatment the chlorid will contain from ninety-eight, to ninety-nine, per cent. of pure magnesium chlorid and may be either fused to a dense crystalline snow-white, or water-white, salt, or be used directly for any required purpose; for instance, it may be used in electrolytic cells for the production of magnesium and chlorid. The treated material is discharged into any suitable receptacle, and wherein any caked lumps, due to incipient fusion, are broken up, while being discharged.

Double salts of magnesium chlorid; such, for instance as carnallite, (the double chlorid of magnesium and potassium) which also crystallizes from its solution with six molecular proportions of water, may, in like manner, be effectively treated by this process, the temperatures and other conditions of treatment being suitably modified for instance, in the case of carnallite, the temperature of the second treatment must not exceed say 400° centigrade, as otherwise fusion will take place.

By this treatment most economical results are produced inasmuch as the whole of the hydrochloric acid employed is recovered, for should even a small portion of acid be removed from the salt during the air treatment this can be readily absorbed by bubbling the escaping air through vessels containing water, and the dilute solution of acid thus obtained can be employed in the absorbing apparatus for the hydrochloric acid plant. It will however usually be found preferable to stop the air treatment before any acid has been liberated.

An example of a suitable arrangement of apparatus for the carrying out of my process is illustrated on Fig. 3, which shows in outline an arrangement of the plant, in a building of two floors, the lower floor containing a pressure blower 1 the air from which passes through a heater 2 into a desiccator 3 and thence into the continuously discharged air drier 4 which is charged with crystals of magnesium chlorid from the upper floor of the building through a hopper at 4^a. Thence the air passes through a tower 5 (which intercepts any hydrochloric acid

present) and escapes, while the charge of partially dried magnesium chlorid is again taken to the upper floor and charged, through a second hopper at 6[a] into the continuously discharged acid-drier 6 from which the finished anhydrous magnesium chlorid produced may be continuously discharged into any suitable vessel. The hydrochloric acid generator 7 furnishes gaseous hydrochloric acid for this acid-drier 6, which gas, after passing through the charge, escapes accompanied by the water eliminated from the crystals and is condensed, in the absorber plant 8, to a nearly saturated solution of hydrochloric acid for reuse, only sufficient water being supplied to the small tower 8[a] of the absorbing plant 8 to produce a concentrated solution from all the hydrochloric acid which is absorbed. In the generator 7 concentrated sulfuric acid is used to again liberate the hydrochloric acid gas, the acid being used at approximately 1.840 specific gravity and discharged from the apparatus at approximately 1.560 specific gravity, at which strength it will be found to contain only approximately three-tenths of one per cent. of hydrochloric acid. 7[a] is a tank for hydrochloric acid and 7[b] is a tank for sulfuric acid. The generator is preferably worked warm (say about 90° centigrade) and a current of air may be employed to expel the last of the hydrochloric acid so that the sulfuric acid can be again concentrated; for instance, in an ordinary cascade concentrator, without the production of objectionable fumes. This operation is very readily carried out. Two generators worked alternately may be provided for each retort.

The process in accordance with my invention is very convenient and economical for use in conjunction with the process described in the specification of my application Ser. No. 317084 for Letters Patent, (of even date herewith) for the simultaneous production of metallic magnesium or its alloys and magnesium chlorate, which in turn is utilized for the production of other by-products, the material produced by my invention being eminently suitable for my improved electrolytic process described in the specification of my application Ser. No. 317803 for Letters Patent of even date herewith.

What I claim is:—

1. In processes for the manufacture of anhydrous magnesium chlorid from the hydrated compound, in which processes hydrochloric acid gas is employed to absorb, or remove, the water of crystallization; partially dehydrating the said hydrated compound so that the temperature of fusion is raised to above 250° centigrade and afterward applying a slow current of hydrochloric acid gas to absorb and remove the remaining water of hydration.

2. In a process in accordance with claim 1; the removal of a portion of the water of hydration by a voluminous current of heated air and following such treatment by the application of a slow current of hydrochloric acid gas, substantially as hereinbefore described.

3. The process in accordance with claim 1, the said process consisting in subjecting hydrated magnesium chlorid to a partial dehydrating process by means of heated air without applying external heat to the charge, completing the dehydrating by means of a slow current of hydrochloric acid gas, with the application of external heat to the charge, and recovering the hydrochloric acid gas by absorption in water.

4. In a process in accordance with claim 1, effecting the preliminary partial dehydration and heating of the hydrated compound solely by means of a very voluminous current of heated air.

5. In a process in accordance with claim 1, carrying out the first stage of the process only until such amount of water has been removed from the initial material that the fusion point is raised to 250° centigrade, or thereabout, and no hydrochloric acid has been liberated.

6. In a process in accordance with claim 1, effecting the preliminary partial dehydration of the hydrated compound by means of a voluminous current of air in desiccated condition.

7. In a process in accordance with claim 1, effecting the preliminary partial dehydration of the hydrated compound by means of a voluminous current of air, halting said dehydration by the current of air before any decomposition, or liberation, of the hydrochloric acid has taken place, and thereafter employing the hydrochloric acid utilized for the main part of the drying process in a cyclic manner by absorbing in water the acid which escapes from the generator to form a strong solution containing all the acid employed and expelling the dry hydrochloric acid from this solution by means of sulfuric acid, substantially as hereinbefore described.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

EDGAR ARTHUR ASHCROFT.

Witnesses:

G. F. TYRON,

L. WALTER.