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ELECTROLYTIC PROCESS FOR THE PRODUCTION OF MAGNESIUM

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The electrolysis of molten chlorides such as those of magnesium, calcium, cerium and similar metallic chlorides, for the production of the corresponding metal, is unfavorably influenced by certain impurities if present in the anhydrous chlorides, and especially by the presence of water, even if the quantity be only very small. As is well known, these chlorides (especially those of Mg and Ce) when in a heated state, and when they contain a small amount of water, decompose, to some extent at least, forming the metal oxide and liberating hydrochloric acid gas. Thus $XMgCl_2+H_2O=MgO+2HCl+(X-1)\ MgCl_2$.

I have now invented a process for the preliminary treatment of such chlorides, by means of which water and any solid impurities (including the oxides of these metals) which may be present, together with their disturbing effects, are easily eliminated, and the energy efficiency of the electrolysis thus greatly increased. The invention comprises the elimination of any water which may be present by decomposing it by a direct electric current under such conditions that not more than a very little of the metallic chlorides are decomposed, while at the same time separating the solid oxides, by allowing them to settle by gravity out of the molten anhydrous chlorides, which for this purpose are kept free from violent agitation.

In what follows the invention will be especially described with respect to treating magnesium chloride, but a few simple and easy experiments will allow anyone skilled in the art to apply it without difficulty to other metallic chlorides of similar nature, such as calcium, cerium, and the like.

The direct and complete dehydration of magnesium chloride is a slow and difficult operation. It has been proposed in the past to dehydrate magnesium chloride by heating lumps of hydrated magnesium chloride in a current of hydrochloric acid gas, or by heating a mixture of potassium and magnesium chlorides to 700 or 800° C. In this way one can fairly easily obtain a nearly completely dehydrated magnesium chloride which however still contains traces of water, and generally about 1 or 2%. Should it however be desired to remove the last traces of water in this way, it would require extreme care and great expense. It has therefore generally been the practice to stop the dehydration at the point above mentioned, but one then has to conduct the electrolysis under conditions which are far removed from the optimum. For if such a chloride still containing water is electrolyzed, at first it is mainly the water which is electrolyzed at the expense of the formation of magnesium. Moreover the current efficiency of the electrolysis is low, the reason for which lies in the fact that the formation of magnesium oxide which is inevitable under such conditions interferes with the electrolysis.

The inventor has discovered that these previously existant difficulties and disadvantages can be overcome in a simple manner if one first electrolyzes out the water in an electrolytic cell before subjecting the now completely anhydrous melt to the main electrolysis. This preliminary electrolysis, which is best carried out in a separate cell prior to the main electrolysis can be carried out by so regulating the current, the voltage, and the time, that the water present is decomposed without decomposing any considerable quantity of the magnesium chloride. The preliminary electrolysis is ended when all the water has been decomposed, after which, the anhydrous melt, after settling out the solid impurities present, is transferred to the main electrolytic cells. In this way one can obtain practically water-free magnesium chloride, which only contains quantities of solid suspensions so small that they no longer interfere with the electrolysis without having resort to complicated and expensive methods.

For this electrolytic elimination of the water one can use electrolytic apparatus of various forms. One can, for instance, carry out the preliminary electrolysis in a cell of the same construction as that serving for the main electrolysis, and using the same current; the water will be decomposed before the chloride, so that dehydration is attained without the formation of more than small quantities of metal. It is however preferable to carry through the electrolysis of the water in the preliminary cell using a current and voltage different from that used for the main electrolysis, and so chosen as to restrict the formation of magnesium to small or negligible amounts. These conditions of current and voltage can naturally vary within wide limits, and also may naturally be such as to require external heat being supplied to the cell serving for the preliminary electrolysis in order to keep the bath molten.

If, for example, a voltage should be chosen of the same order of magnitude as that obtained in the main electrolysis and the current be kept low, the electric energy will be consumed partially in decomposing the water, and partially in keeping the bath hot, the water will be completely de-

composed while so much heat will be generated that it is often unnecessary to supply any external heat to the bath.

Should one however use a high current and a low voltage, preferably lying between that necessary for the decomposition of water and that necessary for the decomposition of magnesium chloride (e. g. about 2 to 2.5 volts), then no magnesium at all will be deposited, the total electric energy will be absorbed in decomposing the water and heating the bath, so that in this case also it is often unnecessary to supply external heat to the bath.

If finally one should use a weak current and a low voltage, there will also be no sensible deposition of metal. In this case however it will be necessary to supply external heat to the bath in order to keep it molten. This method of working has however the added advantage, when one desires to purify the magnesium chloride from solid impurities such as oxide, of causing no movement in the electrolyte, and thus making it easier for the solid suspensions to settle out.

In the following, the discovery will be made clear by means of several practical examples under varying working conditions. In these examples, the water content of the melt was determined in the following way: a sample of the melt was heated with a large excess of magnesium powder, and the quantity of hydrogen liberated determined. From this quantity one can calculate back to the quantity of water originally present. Further during the electrolysis, the quantity of the current which had served to decompose magnesium chloride instead of water was measured as follows: any chlorine in the cell gases was converted into hydrochloric acid, and the total quantity of hydrochloric acid measured as such.

The time to be allowed for the preliminary electrolysis is to some extent dependent upon the nature of the various impurities present in the original magnesium chloride. It will generally be best to control the procedure of the preliminary electrolysis by taking samples of the bath from time to time and testing the amount of water. If the voltage is kept so low that the magnesium chloride cannot be appreciably decomposed, the continuation of the preliminary electrolysis beyond the moment when all the water has been electrolyzed out, will only lead to losses of current; but should a higher voltage be chosen, magnesium will also begin to be deposited. In the latter case a clear sign of the preliminary electrolysis being finished will be the appearance of chlorine.

I have ascertained, during the experiments which led to the present invention, that such double electrolysis will afford a greater amount of metal for an equal consumption of current than by a direct treatment and single electrolysis of magnesium chloride having the same degree of hydration, in a single electrolytic vat.

According to my invention, the deposit of metal during the dehydration or "pre-electrolysis", is limited to a relatively small amount, or there is no deposit in this preliminary operation, this being effected by maintaining the current within certain limits such that the current will be sufficient for an electrolytic decomposition of the water, but will not decompose the metallic chloride or salt, this operation being performed with or without external heating, according to the characteristics of the vat or of the current employed. These characteristics may obviously vary within wide limits. However, I will give three principal examples of the process, as covered by the invention; these are by no means limitative, but are only intended to facilitate the understanding of the present description.

Example 1.—The apparatus is supplied with a small current at a high voltage. By the use of this high voltage, which may have about the same value as is employed for the normal electrolysis, or be considerably higher, there is simultaneously effected an electrolytic decomposition of the water and of the magnesium chloride, but as the current is small, it will be used up, in spite of the high voltage, almost exclusively by the decomposition of the water which is present rather than by electrolysis of the chloride, and the excess energy will be converted into heat. This causes a decomposition of the whole of the water, a small deposit of magnesium, and a supply of internal energy in the form of heat. In this case, it is often unnecessary to supply additional energy by outside heating.

Example 2.—The apparatus is supplied with a heavy current at a low voltage, which latter is preferably kept between the voltage necessary for the electrolytic decomposition of water and the voltage corresponding to the electrolytic decomposition of the chloride. Thus the voltage used may be about 2.0 to 2.5 volts for dehydrating magnesium chloride. Under these conditions there will be no electrolytic decomposition of the chloride, but only an electrolytic decomposition of the water which it contains, and thus the whole of the current is employed for the electrolytic decomposition of the water and also to supply internal energy in the form of heat. In this case as in the preceding, it is often not necessary to supply heat from the outside.

Example 3.—The apparatus is supplied with a small current at a low voltage. As in the second example, this will not effect any appreciable electrolytic decomposition of the chloride, but only the decomposition of the water, especially if the voltage is kept between the values necessary for the decomposition of these two bodies. However in this case an extraneous source of heat is usually required to maintain the bath in the molten state.

This method has a special advantage, since the bath is agitated only to a very small degree during the operation in question, and this furthers the simultaneous use of the method of elimination by settling of the resulting or preexisting oxides.

It should be noted that the aforesaid operations for the preliminary electrolytic decomposition of the water may be employed not only for the dehydration of magnesium chloride, but also for the dehydration of all salts for which the voltages of electrolytic decomposition are sufficiently separated from the decomposition voltage of water.

On the other hand, the operation for the final electrolysis need not immediately follow the preliminary dehydration.

However it appears to the inventor to be particularly advantageous to complete the preliminary dehydration by the complete withdrawal of oxide and other suspensions formed during this process or preexisting, and then to utilize the suspension-free and water-free chloride thus obtained for immediate transference to the vats for the final electrolysis. For this purpose, I effect the separation of the oxides by gravity, the solid impurities being allowed to settle out from the molten chloride in such a manner that only

the pure chloride will be used in the electrolytic vat, while the oxides remain in the settling space or chamber.

This gravity separation may be effected in any suitable apparatus or chambers which are in connection with the vats used for the preliminary or the final electrolysis, or such apparatus or chambers for the decantation may be entirely independent of the vats used for the preliminary or final electrolysis.

It must however be borne in mind that water is only one of the main impurities which interfere with the satisfactory electrolysis of magnesium chloride; the other class of impurities is magnesium and similar oxides, which constitute solid suspensions in the melt.

Such oxides have a tendency to settle to the bottom of the electrolytic cell during the electrolysis, and in this way to carry with them a portion of the magnesium formed, so that frequently a considerable part of the metal may collect at the bottom of the cell instead of collecting together with the rest of the metal on the surface of the melt. This results in appreciable losses in metal. Moreover, since the oxide which settles to the bottom of the cell becomes a conductor owing to the considerable quantity of metal it contains, further losses in the current efficiency of the cell result.

And in addition, the lighter particles of oxide floating as a suspension in the electrolyte attach themselves to the cathode, and may cover this latter with an adherent film of oxide. The presence of this oxide upon the cathode leads to the result that the magnesium is formed in fine particles instead of globules of appreciable size. The metal then disseminates itself in this fine state of division throughout the bath. This again causes two grave disadvantages:

(*a*) The particles are sufficiently fine to allow of recombination taking place between them and the chlorine evolved at the anode, resulting in a great reduction of the current efficiency.

(*b*) Those particles which do collect at the surface of the melt are contaminated with large quantities of electrolyte, making the subsequent purification of the metal much more difficult and costly.

It has so far not been possible, in commercial practice, to wholly avoid the presence of oxide in anhydrous magnesium chloride, even when every possible precaution has been taken in its preparation, because the elimination of water from the hydrated chloride always leads to the formation of some oxide, whereas the direct chlorination of an oxygen-containing compound of magnesium always leaves some unconverted oxide in the product.

By proceeding according to the manner hereinbefore described, it has been found possible greatly to ameliorate the electrolysis of molten magnesium chloride. To this end one subjects the anhydrous chloride to be used for the electrolysis to a preliminary operation during which it is kept quiet in the molten state for a sufficient period of time to permit settling out almost completely the solid impurities, such as oxides. The supernatant purified chloride is then separated from the solid impurities by decantation, and submitted to the electrolysis.

This separation by gravity is preferably carried out in the same vessel which serves for the elimination of any water that may be present, as has previously been described. If particularly desired for any reason, it can also be carried out in a special vessel designed for this purpose only, and which may be situated between the dehydrating device and the electrolytic cell proper.

It is particularly advantageous to carry out the preliminary electrolysis of the water, and the settling out of the oxide which may originally have been present or have been formed during the dehydration, so that the anhydrous chloride free from solid suspensions is immediately transferred to the cell in which the final electrolysis is conducted.

One can for instance transfer the anhydrous chloride after the preliminary electrolysis is terminated into an intermediate receptacle which is joined to the final electrolytic cell in such a way that the heat from the electrolysis is used to keep the chloride molten in the intermediate receptacle. The settling out of the solid suspensions then takes place in this intermediary vessel, where the oxide collects on the bottom, while the purified chloride flows over from the top into the electrolytic cell.

One can also for instance unite the settling out of the solid impurities with the preliminary electrolysis by carrying them out in the same vessel, in which case the current and voltage are so arranged as to impart as little movement to the bath as possible. When the preliminary electrolysis is terminated, the settling out has also practically reached completion, so that a completely water-free and oxide-free melt can be run off from the top of the vessel.

It is needless to add that the settling out of oxide and other solid impurities is not restricted to the case where the water which may be present is removed by a preliminary electrolysis or even to the case where the chloride has simultaneously to be dehydrated.

The following examples, given by way of illustration, will make clear the principles involved.

1—The magnesium chloride, which is wholly or partially dehydrated, is placed in a special chamber communicating with the electrolytic vat, and forming part of this latter in such a manner that it will receive heat from it without the chloride in the settling chamber being subjected to electrolysis. The unfused solids such as the oxide will settle out of the fused chloride in this chamber, and will remain in the lower part of the said chamber. Only the pure decanted chloride taken from the upper part will be transferred to the electrolytic vat and used for the electrolysis properly so called.

2—The settling operation is combined with the operation of fractional electrolytic decomposition wherein all the water is eliminated but only a small amount of metal formed and the bath but slightly agitated, so that the oxides can settle freely to the bottom. When the dehydration is complete, the oxides are practically separated from the melt, and a chloride which is dehydrated and is free from oxides and suspensions can be taken from the upper part of the bath.

It should be noted that this gravity separation is not necessarily in any way connected with the aforesaid operation of dehydration; it may also be effected quite independently of this latter, especially when preparing anhydrous magnesium chloride by the chlorination of a compound which does not contain water. Thus in the case of dry chlorination of an oxygen-containing compound of magnesium, the following method may be used.

The magnesium ore, the reducing agent, and optionally an additional substance or substances

are mixed and formed into blocks, briquettes or the like, and this product is subjected by any suitable process to the action of chlorine or an agent containing chlorine, at the requisite temperature, either above or below the melting point of the resulting chloride or mixture of chlorides or other substances.

After this first operation (or any other operation for the production of an anhydrous chloride by any suitable process) the solid or fused mass is treated in an apparatus which may be provided with heating means, and is brought, either by melting or keeping the mass molten, into a sufficiently fluid state to enable the solid particles in suspension to be deposited under the best conditions. These two operations (chlorination and decantation) can be effected if desired by the continuous outflow of the treated material, or may be performed as specific discontinuous operations.

The chloride in the molten state and free from all solid substances in suspension, is then decanted and is subjected to an electrolysis with or without the addition of any other suitable substance. After a more or less complete separation of the fluid components from the solid deposits, these latter may be again returned, after proper treatment, to the operation of chlorination.

I claim:

1. Process for the electrolytic production of a metal selected from the group consisting of magnesium and cerium, of which the hydrated chlorides are known to be easily decomposed by heat, which comprises the following steps, the order in which steps (*a*) and (*b*) are conducted being immaterial: (*a*) subjecting the incompletely dehydrated metal chloride in a molten state to an electrolytic action which is confined almost exclusively to the electrolysis of water contained in said chloride without formation of any commercial amount of metal; (*b*) allowing settling and sedimentation of solid material heavier than said molten chloride; and thereafter (*c*) separating said molten chloride from said solid material by decantation; and finally (*d*) transferring said purified anhydrous metal chloride into a main electrolytic cell and subjecting the same to final electrolysis.

2. Process as claimed in claim 1, in which the said purified chloride is transferred into the final electrolytic cell in a molten state without having been allowed to solidify at any time subsequent to said purification.

3. Process as claimed in claim 1, in which steps (*a*) and (*b*) are conducted simultaneously.

4. Process as claimed in claim 1, comprising the electrolytic decomposition of water by means of a direct current of an amperage too low for effecting separation of substantial amounts of metal, but at a voltage sufficient to decompose said chloride.

5. Process as claimed in claim 1, comprising the decomposition of water by means of a direct current at a voltage which is above the minimum voltage necessary to decompose said chloride, said current being continued until substantially all the water has been decomposed but being stopped before the separation of substantial amounts of metal is effected.

6. Process as claimed in claim 1, comprising the electrolytic decomposition of water by means of a direct current at a voltage above the minimum decomposition voltage of water but below the decomposition voltage of the salt to be dehydrated.

7. Process for the production of a metal whose hydrated chloride is easily decomposed by heat, such metal being selected from the group consisting of magnesium and cerium, which comprises the following steps: (*a*) firstly subjecting the incompletely dehydrated metal chloride in a molten state to an electrolytic action for decomposing the water by means of a direct current at a voltage above the minimum decomposition voltage of water but below the decomposition voltage of the salt to be dehydrated; (*b*) secondly transferring said dehydrated metal chloride into a main electrolytic cell and there subjecting it to an electrolysis for the production of metal.

8. Process as claimed in claim 1, comprising the electrolytic decomposition of water by means of a direct current of an amperage and at a voltage too low to cause electrolytic separation of metal in substantial amount from said fused chloride.

9. Process for the electrolytic production of metals whose hydrated chlorides are easily decomposed by heat, namely magnesium and cerium, from a bath of molten salts containing the chloride of the metal to be electrolytically separated, which comprises the following steps (*a*) maintaining the bath molten and without any considerable agitation, to allow the solid impurities to separate by gravity from said bath; (*b*) removing the supernatant fused melt by decantation from the solid residue; (*c*) and conveying the decanted material into an electrolytic cell for electrolysis thereof.

10. Process for the electrolytic production of metals whose hydrated chlorides are easily decomposed by heat, namely magnesium and cerium, from a bath of molten salts containing the chloride of the metal to be electrolytically separated, which comprises the following steps, the order in which steps (*a*) and (*b*) are conducted being immaterial: (*a*) maintaining the bath molten and without any considerable agitation, to allow the solid impurities to separate by gravity from said bath; (*b*) passing an electric current through the melt without formation of metal by electrolysis; (*c*) and finally transferring said chloride after separation from said solid material into an electrolytic cell and there subjecting it to electrolysis for the production of metal.

11. Process for the electrolytic production of a metal selected from the group consisting of magnesium and cerium, from a molten salt bath containing the chloride of such metal, which comprises the following steps, the order in which steps (*a*) and (*b*) are conducted being immaterial: (*a*) maintaining the bath molten and without any considerable agitation, to allow the solid impurities to separate by gravity from said bath; (*b*) passing an electric current through the melt without formation of any commercial amount of metal; (*c*) and finally transferring said chloride after separation from said solid material into the main electrolytic cell and there subjecting the same to final electrolysis.

12. Process for the electrolytic production of a metal selected from the group consisting of magnesium and cerium, from a bath of molten salts containing the chloride of the said metal, which comprises the following steps conducted in the following order: (*a*) passing an electric current through the melt without formation of metal; (*b*) maintaining the molten bath without any considerable agitation, to allow the solid impurities to separate by gravity from said bath; (*c*) transferring said chloride after separation from said solid material into a main electrolytic

cell and then subjecting it to electrolysis for the production of metal.

13. Process for the electrolytic production of a metal selected from the group consisting of magnesium and cerium, the hydrated chlorides of which are easily decomposed by heat, from a bath of molten salts containing the chloride of one of these metal chlorides, which comprises the following steps: (*a*) applying a source of heat sufficient to maintain the bath molten; (*b*) maintaining the molten bath without any considerable agitation, to allow the solid impurities to separate by gravity from said bath; (*c*) and finally transferring said chloride after separation from said solid material into an electrolytic cell and there subjecting it to electrolysis for the production of metal.

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