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ELECTROLYTIC PREPARATION OF MANGANESE

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This invention relates to improvements in the electrowinning of manganese metal from chloride solutions and more particularly to a process characterized by the formation of high purity manganese metal with the simultaneous recovery of concentrated chlorine suitable for liquefaction, avoiding the formation of manganese dioxide.

In commercial practices for electrowinning manganese metal, a manganous sulfate electrolyte has been used. Usually the fresh or recycle electrolyte feed is introduced into a catholyte chamber, manganese is precipitated on the cathode and the catholyte flows through a diaphragm into the anolyte compartment. Manganese dioxide is deposited on the anode and the depleted anolyte is removed for fortification and purification before recycling to the catholyte chamber.

It has also been proposed to electrolyze manganese chloride electrolytes containing ammonium chloride (see for example Bureau of Mines Report of Investigations 4817). The process appears to have several advantages over the sulfate electrolysis, particularly in lower cell potential which reduces power consumption by 25%, better recovery of manganese, easier preparation of the electrolyte, longer periods of deposition, which reduce the cost of handling cathodes, and the avoidance of manganese dioxide deposition at the anode. A serious objection to the commercial feasibility of the process, however, is the consumption of ammonia due to reaction of liberated chlorine with ammonium ions in the electrolyte. Nitrogen together with some chloramines are evolved and the gas may contain as much as 1% of chlorine. Not only is the chlorine wasted but ammonia is decomposed and must be replaced in the electrolyte before it can be recirculated resulting in high operating costs.

My invention provides means for the electrolysis of manganous chloride solutions to obtain manganese in high yields and desirable form at low cell potentials in a process in which concentrated chlorine is recovered as an anodic product and in which losses of nitrogen are negligible. In the practice of my invention, separate catholyte and anolyte solutions are employed. The solutions are separately circulated to the cell, removed, fortified and recirculated to their respective cathode and anode compartments. The catholyte contains manganous chloride and ammonium chloride in aqueous solution. The manganese released can be deposited on stainless steel or other suitable cathodes. Substantially no loss of ammonium chloride occurs, and the effluent catholyte is refortified with manganese chloride and recycled to the catholyte compartment. The anolyte solution contains a soluble chloride, preferably hydrochloric acid or an alkali or alkaline earth chloride. The anolyte is maintained free of ammonium ions, for example, by mechanical flow of anolyte to the catholyte compartment, and chlorine substantially free from other gases except moisture is liberated at the anode. The effluent anolyte

is refortified with acid or salt and returned to the anolyte compartment.

The anolyte and catholyte compartments are suitably separated by a diaphragm. Conduction through the diaphragm occurs by means of the migration of sodium and/or hydrogen ions from the anolyte to the catholyte and by chloride ions and hydroxyl ions from catholyte to anolyte. The catholyte contains a high concentration of chloride ions which therefore carry most of the current towards the anolyte. The head of the anolyte is adjusted so that the mechanical flow of anolyte through the diaphragm is sufficient to hold back cations, i. e., the ammonium ion, which could otherwise diffuse through the diaphragm, but insufficient to prevent the electrolytic migration of anions into the anolyte. When waste hydrochloric acid is used as anolyte, hydrogen ions are the current carrying means from anolyte to catholyte. When a sodium chloride brine is used as anolyte or the anolyte contains appreciable quantities of sodium ions, they will be transferred through the diaphragm and will accumulate in the catholyte. In the latter case, effluent catholyte can be advantageously cooled to crystallize excess sodium chloride from solution during the recycling of the catholyte. The use of hydrochloric acid as anolyte is advantageous since it eliminates the need for a crystallization or other salt-removing operation. With hydrochloric acid as the anolyte, it is necessary only to fortify the catholyte in manganese chloride and adjust the pH before returning it to the catholyte compartment.

Although the catholyte liquor may be prepared and fortified with pure manganese chloride and pure ammonium chloride or mixtures thereof, the manganous chloride employed usually is derived from a manganese ore, for example, manganese carbonate, so that suitable purification before introduction to the cell is required. Impurities such as calcium, magnesium and iron are likely to be present as well as minor proportions of copper and cobalt. These may be largely removed by the introduction of a soluble sulfide such as sodium sulfide or preferably hydrogen sulfide. The latter reagent avoids the introduction of sodium ions. The addition of ammonia serves to precipitate iron and other hydroxides. The precipitated impurities are suitably removed by settling and/or filtration, and the catholyte feed is brought to a pH of about 7 by the addition of hydrochloric acid.

The catholyte feed is preferably such as to maintain concentrations in the catholyte chamber of about 6 to 15 grams per liter of manganous ion and 90 to 130 grams per liter of ammonium chloride. The ammonium chloride increases the conductivity of catholyte, acts as a buffering agent and prevents precipitation of manganese within the cell as the hydroxide. Also it appears to improve the electro deposition of the manganese at the cathodes. The addition of small amounts of sulfur dioxide to the catholyte helps to prevent oxidation of the manganese metal and to avoid the formation of manganese dioxide. About 0.05 to about 0.5 gram per liter of sulfur dioxide may be used although ordinarily about 0.1 gram per liter is sufficient. Sodium thiosulfate or other equivalent of sulfur dioxide may be substituted, but sulfur dioxide itself is generally preferable since it avoids the introduction of sodium ions.

The anolyte comprises hydrochloric acid or an alkali or alkaline earth metal chloride, e. g. sodium, potassium or calcium chloride. Preferably, it contains hydrochloric acid in a concentration of about 30 to 33%. The concentration is maintained by any suitable means, usually by the introduction of hydrochloric acid. Pure, concentrated hydrochloric acid can be added to the anolyte compartment or by-product hydrogen chloride can be dissolved in spent anolyte to fortify it. Where sodium

chloride or other salt brines are used as anolyte, the latter can be fortified by the continuous or intermittent addition of more concentrated brines to the anolyte compartment. Such brines need not be extremely pure since the ions transferred to the catholyte through the diaphragm are removed in the purification of the catholyte during the recycling operation.

The rate of feed to the anolyte is adjusted to keep ammonium ions out of the anode compartment and is dependent on the efficiency of the diaphragm in this respect. About one-sixteenth inch or more, preferably about one-eighth inch, of hydrostatic head in the anolyte compartment is sufficient to accomplish this result with most diaphragms. A small flow is sufficient since ion diffusion in solution is extremely slow. A greater head can be applied if less porous diaphragms are employed, for example, a felt-like Dynel (a cloth woven from filaments comprising copolymers of acrylonitrile and vinyl chloride) diaphragm, since the low porosity prevents excessive flow of anolyte to catholyte. The most advantageous method of maintaining a proper head of such small dimensions is by maintaining a constant overflow in the electrode compartments. Constant recirculation of the electrolytes with proper concentration adjustments outside of the cell insures a homogeneous feed to each cell compartment. A fixed overflow in each compartment insures the proper liquid level in each electrode compartment when the feed is greater than consumption of electrolyte due to electrolytic decomposition.

The cell preferably comprises a plurality of anode and cathode compartments separated by suitable diaphragms. Because of the acidity in the anolyte, materials resistant to hydrochloric acid and chlorine are required as diaphragm materials. Vinyon (a cloth woven from polyvinyl chloride filaments) is a particularly suitable material for this purpose. The diaphragm must be porous enough to allow a small flow of anolyte to the catholyte compartment and yet dense enough to prevent back diffusion of the catholyte. The anodes can be graphite and the cathodes can be stainless steel or titanium. A cell potential of about 3.5 to 3.6 volts can be applied using, for example, a current density of about 45 to 50 amperes per square foot. The temperature of the cell advantageously is maintained at about 35–40° C. Suitable cooling means are provided for the cell such as jackets carrying cooling water or coils of glass within the cell.

From time to time, for example after about 36 to 48 hours, individual cathodes are lifted from the cell for manganese removal. In order to facilitate the operation, stainless steel cathodes before use are advantageously dipped in a dilute sodium silicate solution followed by thorough spray rinsing. This reduces adhesion so that the manganese metal can be readily removed by flexing or rapping with a rubber mallet. The cathodes advantageously can be buffed occasionally to maintain a relatively smooth finish on the surface. With titanium cathodes, however, it is advantageous to roughen the surface with emery cloth before use in order to improve the adhesion of the deposited manganese until the cathode is removed from the cell.

The effluent chlorine gas from the anodes is collected and since it is saturated with moisture, it is dried in conventional ways. For example, the effluent gas can be dried by scrubbing with concentrated sulfuric acid after which it can be compressed and sold or utilized in any desired manner.

A particular advantage of the new process is that it makes use of manganous chloride which is readily obtainable from low grade manganese ores. Manganese is recovered as metal and chlorine is produced as liquefiable gas without corresponding production of caustic. No fixed nitrogen is lost as in previous operations since the anolyte is maintained free of ammonium ions.

The process of my invention will be further illustrated by reference to the following examples.

Example I

A cell having three electrodes was equipped with two diaphragms to isolate each electrode in its own compartment. The center cathode was stainless steel, while the two outer anodes were of graphite. The diaphragm material was Vinyon–1424N, a woven polyvinyl chloride cloth. Each compartment had a volume of about 200 milliliters.

The three compartments were fed with electrolyte at the bottom and were equipped with overflow tubes at the top. In this way the anolyte level was maintained from about 1/16–1/8 of an inch above the catholyte level. Flowmeters were inserted into each feed line to measure the flow of electrolyte into each compartment.

The anode compartments were filled with a substantially saturated solution of sodium chloride, while the cathode compartment was charged with an aqueous solution containing 6.0 grams per liter of manganous chloride. The pH of the latter solution was 7.7.

A potential of 3.6 volts was applied to the electrodes, causing a current of 3.0 amperes to flow through the cell. At the same time the anode compartments were fed with a substantially saturated solution of sodium chloride at the rate of about ½ to 1 milliliter per minute. The cathode compartment was fed at the rate of about ½ milliliter per minute with an aqueous solution containing 53.2 grams per liter of manganous chloride and 110 grams per liter of ammonium chloride. The pH of this latter solution was 6.7 after being purified by the addition of minor amounts of $Na_2S_2O_3$ and SO_2.

The cell was operated in this manner for 7 hours at a temperature of about 35° C. At the end of this time a good deposit of 12.9 grams of manganese, on the cathode, indicated a current efficiency of 60 percent. Only chlorine was formed at the anodes, and this partially dissolved in the anolyte and partially escaped to the atmosphere. No ammonium ions appeared in the anolyte and no nitrogen or nitrogen chlorides appeared in the chlorine.

Example II

The cell described in the first two paragraphs of Example I was again used.

The anode compartments were filled with a substantially saturated solution of sodium chloride, and the cathode compartment was filled with an aqueous solution of 14.4 grams per liter of manganous chloride having a pH of 6.7.

A potential of 3.5 volts was applied to the electrodes causing 3.0 amperes to flow through the cell. The cell was fed the same electrolyte solutions as were used in Example I, and at the same flow rates. At the end of 4½ hours a firm deposit of 9.4 grams of manganese indicated a current efficiency of 67.8 percent. The higher current efficiency in this case was due to the shorter operating time. No ammonium ions appeared in the anolyte and no nitrogen or nitrogen chlorides appeared in the evolved chlorine.

This application is a continuation-in-part of my pending application Serial No. 301,390, filed July 28, 1952.

I claim:

1. An electrolytic process for the production of manganese metal and chlorine from manganous chloride which comprises introducing, withdrawing, fortifying and returning an aqueous catholyte solution containing manganous chloride and ammonium chloride to a compartment of a dual electrolyte cell having an anode and a cathode in separate compartments separated by a diaphragm, introducing, withdrawing, fortifying and returning an aqueous anolyte solution consisting essentially of a solution of soluble chloride selected from the group consisting of hydrogen chloride and alkali and alkaline earth metal chlorides to an anode compartment of the cell, establish-

ing electrical conduction through the cell by application of an electric potential to deposit manganese metal at the cathode and to discharge chlorine gas at the anode while maintaining the anolyte substantially free of ammonium ions.

2. The process of claim 1 in which a hydrostatic level in the anolyte compartment above the level in the catholyte compartment is maintained.

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