

The Electrolysis of Fused Manganese Chloride

by

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To Dr. A. N. Campbell who suggested the problem dealt with herein, and who directed and very kindly assisted in this work, the thanks and appreciation of the writer are offered.

(1) Theoretical Introduction.

Molten salts are good conductors of electricity and their conductivity is of an electrolytic nature. In considering the subject of conduction in fused electrolytes, it may be said at the outset, that compared with the carefully elaborated and well verified theory of electrical conduction in aqueous solutions, the present state of our knowledge is very incomplete. This is due in part to experimental difficulties which are inherent in the accurate measurement at high temperatures of properties whose large temperature coefficients demand the establishment and measurement of temperature to within a few tenths of a degree. Until comparatively recently, data on such properties as the density, specific conductance, and viscosity of fused salts, which were reliable to a few tenths of a percent, were not available, and even yet, much still remains to be accomplished in this field. Aside from experimental difficulties there are also theoretical difficulties presented by fused electrolytes, which render conclusions regarding their constitution more difficult than in the case of aqueous conductors.

In the electrolysis of molten salts the products liberated at the anode and cathode are the ones we should expect to result, and are analagous to those from aqueous solutions. For example, lead chloride gives lead and chlorine, sodium chloride gives sodium and chlorine and sodium nitrate gives sodium together with oxygen and nitrous gases. The specific conductivity of

a number of fused salts, at temperatures a few degrees above their melting points are given in table I (1).

TABLE I

<u>SALT</u>	<u>TEMP. DEG. C.</u>	<u>(K RECIP. OHMS PER SQ. CM.)</u>
NaNO <sub>3</sub>	318	1.022
KNO <sub>3</sub>	343	0.645
CaCl <sub>2</sub> (M. P. 774)	800	1.90
K <sub>2</sub> CO <sub>3</sub>	900	1.95
ZnCl <sub>2</sub> (nearly pure)	300	0.00186
PbCl <sub>2</sub> (impure)	520	1.596
NaCl(M. P. 800)	850	3.50

Comparison of the above figures with a table of conductivities of aqueous solutions at 18 C. show that the conductivity of molten salts are of the same order although usually considerably greater. The conductivity increases considerably with rise in temperature, indeed in an almost linear manner with the rise in temperature over a moderate range. The decrease in the viscosity of the melt is believed to explain the temperature effect in most cases.

Table II and III give results obtained by Lorenz and Kalmus (2) and Aradt and Gessler (3).

TABLE II

<u>K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(L &amp; K)</u>		<u>NaNO<sub>3</sub>(L &amp; K)</u>	
<u>g</u>	<u>k</u>	<u>g</u>	<u>k</u>
397	0.1959	308	0.965
407	0.2198	318	1.022
417	0.2381	328	1.065
437	0.2745	338	1.108
457	0.3109	348	1.151
477	0.3473	358	1.195
497	0.3837	368	1.239
507	0.4019	378	1.283

TABLE III

<u>AgBr(A &amp; G)</u>		<u>CaCl<sub>2</sub>(A &amp; G)</u>	
<u>g</u>	<u>k</u>	<u>g</u>	<u>k</u>
450	2.93	800	1.90
500	3.02	850	2.12
550	3.10	900	2.32
600	3.18	950	2.50
700	3.34	1000	2.66
800	3.50	1050	2.76
900	3.68		

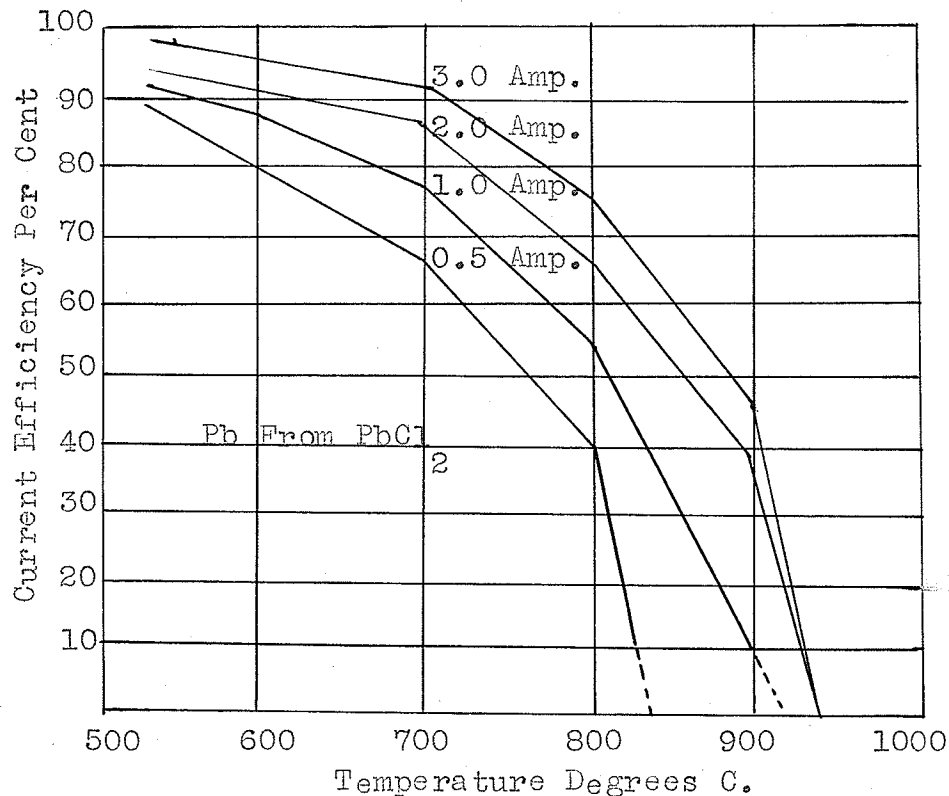
The conductivity of a fused salt mixture is usually lower than that calculated from the mixture law, and sometimes falls below that of any of the pure components.

Current Efficiency.- It has been rigorously proven by Lorenz and Helfenstein (4) and Richard and Stull (5) that Faraday's law is valid for the electrolysis of molten salts. The factors which cause lowering of current efficiencies at room temperature are far more active at higher temperatures. The velocity of chemical reaction and the velocity of diffusion being much greater. As a result the yields obtained will be less than those calculated from Faraday's law unless the anodic and cathodic products are carefully separated from each other and from the action of the atmosphere and the electrolyte. The chief sources of cathodic metal loss in the electrolysis of molten salts are volatility, diffusion of anode products to the cathode, formation of metal fog, and the oxidizing effect of the atmosphere. The yield declines rapidly with increase in temperature. This is shown in figure I where the different curves hold for different current densities. The reason that increase in current density increases the current efficiency is simply due to the fact that with increase of current density the amount of cathode product produced in unit time increases much more rapidly than the absolute losses of the cathode product from increasing diffusion from the anode, therefore the current efficiency rises. The efficiency may fall to zero at very low current densities because the amount of cathodic product formed in a unit of time may not exceed the amount consumed by the



different sources of loss. The increase of current density

FIGURE I



is only limited by voltage considerations, the development of Joule heat near the electrodes, and by the anode effect which causes an unusual rise of voltage. Occasionally, losses may arise due to the formation of a sub salt between the precipitated metal and the melt. Under certain conditions in the electrolysis of calcium chloride this occurs; red crystals of calcium chloride are produced. In unusual cases the metal may dissolve in the electrolyte as in the case of molten sodium hydroxide to form a true solution.

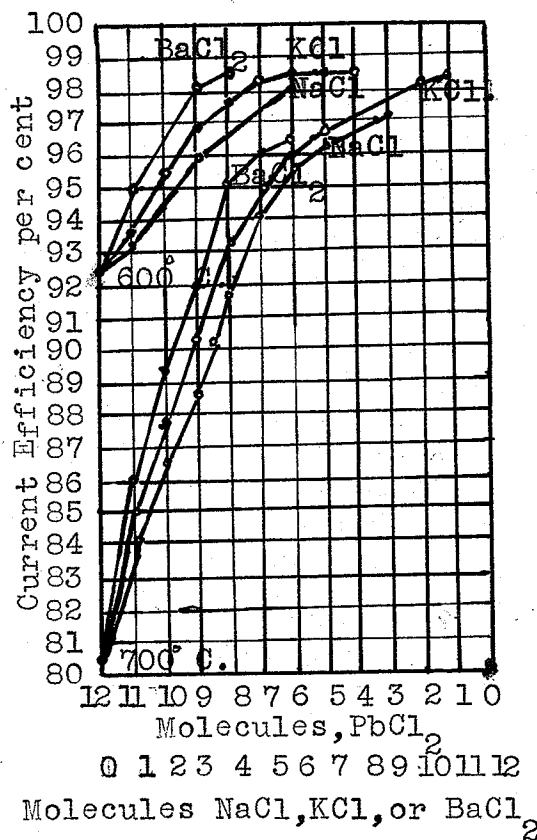
Metal Fog.- The formation of metal fogs is a source of loss peculiar to molten electrolytes. If a metal such as zinc or lead is melted under one of its fused salts, the salt will have little effect on the metal if the temperature be near the melting point of the salt. If the temperature be raised however, there is an apparent tendency of the metal to dissolve in the melt and dark clouds rise up from the metal. This continues until a state of equilibrium is reached. With decrease in temperature the metal fog produced slowly settles down and finally re-enters the metal. These metal fogs may markedly color the electrolyte. With lead in lead chloride a yellow melt results and at higher temperatures a brown one. If the excess of massive metal be removed, and air kept excluded, the colored melt appears stable. The admission of traces of oxygen or an oxidizing agent will cause the color to disappear. The effect however, can be produced by the admission of a reducing agent.

Essentially the same phenomena must occur during the electrolysis of molten salts, and it will adversely affect the yield, because while it is true that only a small quantity of metal is present in such melts, less than 0.1 percent (C), the metal in this state is much more active chemically than the massive metal and it diffuses rapidly through the melt to the anode where it recombines with the anode product. The colloidal nature of these fogs have

been proven by Lorenz and Eitel (7).

The addition of certain neutral salts prevents the formation of fog just as the addition of electrolytes to an aqueous colloidal solution may precipitate the colloid. The mode of action in the two can hardly be the same however. Several theories have been advanced for this action of neutral salts. Their action can be

FIGURE II



studied by measuring their effect on cathodic current

efficiencies during electrolysis. As the fog formation is one of the chief sources of loss of current efficiency, the two effects will run more or less parallel. Figure II will illustrate the influence of the addition of different salts on the course of electrolysis of molten lead chloride. In cases where the electrolysis loss under normal conditions are greater, the effects produced are even more marked. The addition of the electrolyte does not always increase the current efficiency. For example, if ferric chloride be added to lead chloride the yield diminishes considerably, even if the addition be very small.

In this connection Appelberg (9) gives the following figures:

TABLE IV.

PbCl<sub>2</sub> at 600 C.

<u>% FeCl<sub>2</sub></u>	<u>CURRENT EFFICIENCY</u>
0.0	96.3
0.005	95.6
0.03	87.6
0.10	76.8
0.40	70.5
0.80	51.7
1.6	22.3
3.2	19.8

The results shown here can probably be explained by the Ferric

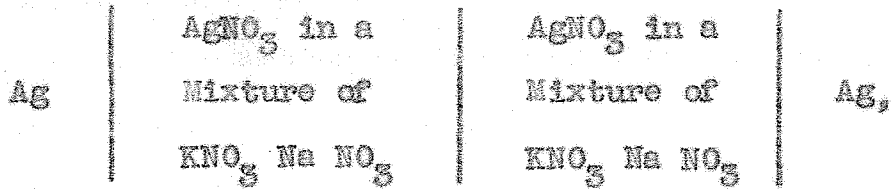
chloride being reduced at the cathode, either electrolytically or by the action of the metal fog, and being reoxidised at the anode. It can be readily seen that traces of impurities entering the melt from the containing apparatus may greatly affect the result.

In connection with manganese it is to be noted that Lorenz (10) in his discussion of the method of preparing manganese patented by L. Volmer (11) remarks that the addition of the alkali chlorides causes a reduction in the manganese content to occur particularly at the cathode. Neither does he recommend the addition of the alkali earth chlorides.

Decomposition Voltage.— With pure fused salts, unlike aqueous solutions, the electromotive force does not depend on the concentration, as this factor does not enter. The reversible electromotive force of the cell depends only on the nature of the electrode, electrolyte and temperature. The decomposition potential varies in a like manner. The two obviously will be equal. For example, the decomposition voltage of fused lead chloride at 570 C. is 1.250 volts, while the electromotive force of the cell

Pb | PbCl<sub>2</sub> | Cl<sub>2</sub> at the same temperature is 1.240 volts. With  
       | fused |

mixtures of salt the electromotive force will depend upon the concentration of the salts corresponding to the metals used as the electrodes. For example, Gordon (12) measured cells made up as follows:



the silver nitrate concentration in the melts surrounding the two electrodes being different. He found that the electromotive forces of such cells could be expressed by the formulae for concentration cells:

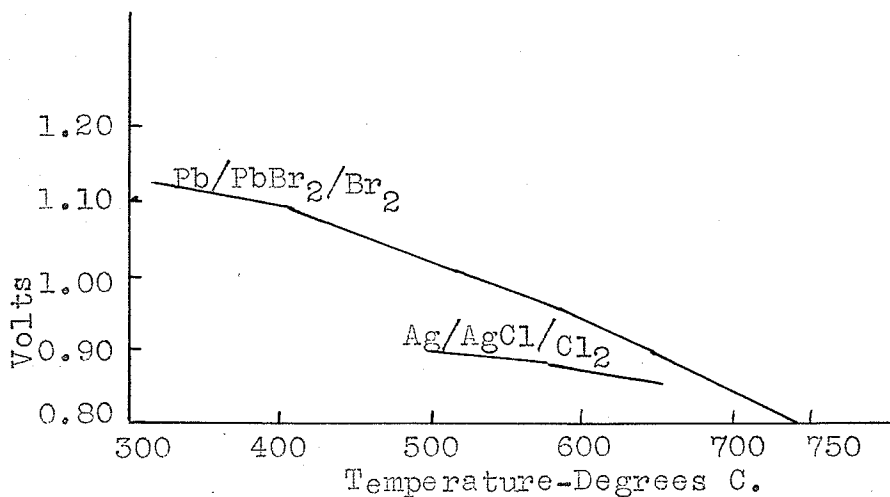
$$E = \frac{0.0002T}{n} \log \frac{(C_1)}{(C_2)}$$

where  $n$  in this case is one and  $(C_1)$  &  $(C_2)$  are the molecular concentrations of the silver nitrate.

In primary cells the reversible electromotive force is a measure of the work furnished by the corresponding chemical reaction. This varies with temperature and as with fused salts a large range of working temperature is possible, there is a correspondingly large range of electromotive force or decomposition potential. In the electrolytic processes corresponding to the reaction fused salt  $\rightarrow$  metal + halogen or non metal, the electromotive force falls as the temperature rises, corresponding to the tendency of the melt to dissociate more and more with rise in temperature. Therefore the free energy liberated during the combination of its constituents becomes less. For example, take the cells

$\text{Ag} | \text{AgCl}_2 | \text{Cl}_2$  and  $\text{Pb} | \text{PbBr}_2 | \text{Br}_2$  (13). This is plotted in Figure III.

FIGURE III



From the view point of the necessary voltage at least, it would be advantageous in the case of fused salts to use as high a temperature as possible. The disadvantages of high temperatures however, are in the increased wear and tear of the plant, decreased current efficiencies, increased difficulty of operation and by the heat expenditure necessary to compensate for radiation losses. These defects more than offset the advantages of higher temperatures.

Polarization and Anode Effect.- With fused salts irreversible voltage effects etc., are far less important than with aqueous solutions. Such effects ultimately depend on the low velocity of some stage of the electrode process, and in view of the known effect of temperature on reaction velocity, it is natural that at high temperatures they should be in general very slight, but nevertheless, when the current density becomes high they make their appearance. Without any obvious external cause, the voltage suddenly increases markedly, the amperage decreases, a soft rustling hissing sound is heard like the discharge of a small induction coil, and the anode seems to be covered by myriads of little luminous spark discharges. The molten electrolyte which has been in close contact with the anode shrinks away from it and does not appear to wet it. The normal evolution of gas around the anode ceases. These phenomena are all summed up in the term "Anode Effect."

There are other effects also which occur at the same time, although these appear to result from the anode effect rather than aid it. If the anode effect occurs with a fairly high frequency, rheostats and busbars in the circuit may rattle and vibrate, or, if the frequency be high enough give off a musical note. These sounds always give warning that the anode effect is occurring in the fused electrolyte.



On account of the high resistance and the numerous small arcs the anode and electrolyte in its immediate vicinity become much overheated. This overheating causes the anode to burn off much more rapidly, sometimes above the level of the melt, and may cause a much lower yield of product. This means in commercial installations a large consumption of unused power.

During the normal course of electrolysis the anode is surrounded by gas bubbles which are constantly escaping from it. They seem to form at the anode and escape easily from it. The moment the anode effect occurs the electrode becomes covered with a film of gas, -  $\text{Cl}_2$ ,  $\text{F}_2$ ,  $\text{Br}_2$ , or  $\text{I}_2$ , - through which the current can only pass as an arc discharge. This covers the anode and by pushing the electrolyte away produces the "non-wetting" effect of the anode. The voltage rises very considerably, and the anode appears to glow because of the large number of tiny arcs which are passing. Complete interruption of the current does not occur.

Mantell (14) has summed up the present state of knowledge about the causes of the anode effect in the following paragraphs.

"The experimental observations and explanations of those who have studied the anode effect appear complex and confusing. They all seem, nevertheless, to fit into a broad, general view of the phenomenon. The detailed explanation in any particular case may differ from that in other cases.

What seems to be a cause in one case may be an effect in another."

"Assume first that the anode effect is the formation of a gas film surrounding substantial portions of the anode. The film prevents the electrolyte from wetting the anode. The result is observed in the formation of myriads of tiny arcs, since the current must pass from anode to electrolyte through the gas film. Once the gas film has been established, it tends to perpetuate itself, since the arcing generates an excessive amount of localized heat which causes the gas to expand. There is then a considerably higher voltage drop from the anode to bath. This involves a greater expenditure of power, and tends also to maintain the anode effect."

"The factors which interrupt the regular normal evolution of gas at the anode by causing the formation of a high resistance gas film may be many. They may vary from time to time in the same electrolytic operation. Any condition which tends to produce a local overheating on the surface of the anode may start a train of events which results in the anode effect. A high resistance film of solid material may form on the anode surface. This film may consist of impurities left on the surface of the anode by the continued consumption of carbonaceous material; it may consist of some relatively insoluble constituent of the electrolyte which has migrated to the anode and adhered to it, or it may consist simply of frozen electrolyte which has become attached to

the anode through local cooling of the bath."

"As this high resistance film forms, the current density increases in other areas, the voltage drop and the expenditure of power increase, and local overheating may start the formation of an anode effect (gas film) at one or two points. Too high a current density may be an important factor in providing the initial impetus for the anode effect. Moreover, either too hot or too cold an electrolyte may start the anode effect. Too cold an electrolyte may cause freezing on parts of the anode surface, increasing the current density on other parts. Too hot an electrolyte will bring operations into a field which is sensitive to the anode effect."

"Surface tension plays a part in the delicate balance between wetting and non-wetting of the anode by the electrolyte. In some cases an electrolyte of high viscosity might permit the retention on the anode of solid material which would start the local overheating."

"The anode effect will disappear, of course, when the surface of the anode is cooled, or the current density so reduced that the gas film collapses and the normal evolution of gas is resumed. It will not reoccur until a certain combination of circumstances permits the re-establishment of the high resistance film."

"The anodic current density above which the anode effect will occur will vary with the nature of the electrolysis and the temperature. They average about 4 to 5

amperes per square cm. with hard carbon and 7 to 8 amperes per square cm. with graphite. The phenomenon has been observed with chlorides of lead, cadmium, silver, sodium, potassium, calcium, strontium, barium, magnesium, cerium, aluminum; with bromides of silver and lead; with lead iodide; and with aluminum fluoride, sodium beryllium fluoride, and sodium aluminum fluoride (15). It is most pronounced with fluorides, least so with iodides. It may be accompanied by a weight loss of the anodes through the formation of halides of carbon, which increases with current density and with temperature."

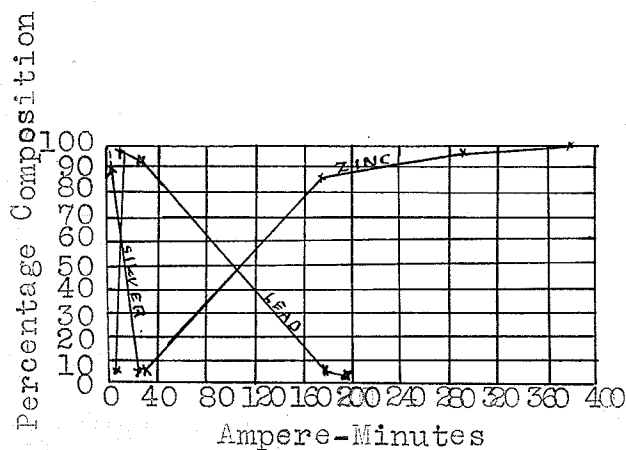
The only other appreciable irreversible effect is the "concentration polarization" which occurs at high current densities. A part from any formation of gas layer on the electrode, the voltage of a working cell increases with current density, just as with aqueous electrolytes. In the latter case the cause is exhaustion of ions near the electrode, and if we assume the presence of ions in molten salts, we can suppose the same cause to be active there.

The reversible electromotive force of a cell can be determined by either decomposition voltage or polarization discharge methods. In the latter case, the curve falls far more rapidly than a similar curve got with an aqueous electrolyte, owing to the high temperature and the rapid rate of diffusion of products away from the electrodes.

Owing to the differences in decomposition potential shown

by different fused salts, a separation of several metallic constituents from a mixture is possible in the molten state, just as in aqueous solution. The relations of course may be rendered rather complex by the varying tendencies of the metals to alloy amongst themselves and thus to depolarise one another's discharge. Figure IV shows the results obtained by Lorenz (15) from a mixture of the chlorides of

FIGURE IV



silver, lead, and zinc. The abscissae represent the quantity of electricity passed since the beginning of electrolysis, and the ordinates the composition of the cathode product removed from the cell at the corresponding intervals of time. The silver is preferentially deposited, then lead, finally zinc.

Electrolysis, - Lorenz' investigations of many fused

electrolytes (17) showed that their behaviour differs from that of dilute aqueous solutions in a number of respects. The equilibria between fused salts and molten metal have been studied recently by Lorenz and Fraenkel (18). The effects of diluents to the salt phase and to the metal phase in various reactions has been recorded by them. They show that the results obtained depend on whether or not the diluent be a strictly indifferent salt or metal. Lorenz found that the law of mass action does not hold for fused electrolytes, and developed a modified equation of the law of mass action which does apply to condensed systems.

(2) History.

Although a great deal of work has been done on the electrolysis of the fused salts of many metals, a search through the literature shows that up to the present the electrolysis of the fused salts of manganese has not been nearly as thoroughly studied as that of other metals, e.g. aluminum. This possibly is due to the fact that commercially pure manganese is not in great demand, its alloys, especially ferro-manganese, being of much greater importance, and these are generally prepared by the use of manganese ores, not the metal itself.

Faraday was the first to show that manganese chloride conducted an electric current when in a molten state (19).

His work was followed by L. Volmer (20), who in 1892 patented an apparatus for the production of manganese by the electrolysis of the fused melt. According to the patent the pure metal which was free from the ordinary technical impurities, e.g. Fe, Si, P, S, and C, was obtained from molten manganese chloride or fluoride. It was impossible to avoid a certain amount of manganese oxides in the melt, these being formed secondarily during the electrolysis. It is stated that during electrolysis additions of manganese oxides can be made without harmful influence on the process, the oxide being transformed into chloride by the evolved chlorine. The salts are worked at the melting temperatures lying just below red heat. In place of ordinary carbon anodes, anodes mixed with any manganese oxide and as much carbon as will unite with the



oxygen from the manganese oxides were used. The manganese collected as a crystalline powder in a metal vessel placed at the bottom of the metal melting crucible and was removed by pulling out this vessel. After this, it was freed from the admixed melt by pressing in the hot stage or washing.

If it is desired to obtain the manganese directly in the form of an alloy, the metal vessel above mentioned is filled with the metal in question. Other apparatus also, of refractory material can be used in place of the metal melting crucible. The electrolysis can be carried on without the addition of manganese oxides.

Fredrick Krupp of Essen, Germany (21), patented an electrolytic apparatus for the preparation of pure chromium, manganese, and their alloys. The molten chloride compounds of the alkalis were submitted to electrolysis, metals or metal alloys being used as an anode which were then dissolved by the discharged chlorine to form chlorides, which passed into the melt. The sodium deposited from the cathode burns however, and makes the melt alkaline, so that the metallic chlorides decompose and precipitate as oxide. Hence, it is necessary to provide for separation of the cathode and anode spaces, either by porcelain cells around the cathode, or by diaphragms, or by carrying out the electrolysis in a U shaped vessel of refractory material, or else one attempts by sufficient heating to evaporate the sodium continuously at the cathode. The metal chlorides produced are then able to form

without disturbance at the anode. The sodium can also be removed by transforming it back into sodium chloride with a stream of chlorine, either during the electrolysis or afterwards. As soon as a sufficient quantity of the metal chloride has been formed and the sodium separated at the cathode, the porous cell is pulled out and chlorine is let into the cathode space. The pure metals or their alloys can now be deposited at the cathode while simultaneously new quantities of chlorine are formed from the metal forming the positive pole, and in such a manner that the composition of the bath remains constant. In this way the metal or metallic alloy is obtained in pure form at the cathode from an impure crude metal containing carbon. Thus, for example, pure carbon free ferro-manganese and ferro-chromium are produced from the impure ferro-manganese and ferro-chromium of commerce. In the same way all other metals and alloys can be brought to a high degree of purity by this method.

If from the start one has a sufficient quantity of chloride, or a corresponding halide compound, for the formation of the bath to provide the protecting products for the electrolysis, the bath can be prepared at once of the necessary concentration, and metal deposition can be proceeded with at once. It is also possible in the case of some readily fusible and difficultly volatile metal chlorides to do away entirely with alkali chlorides and use the

former alone as electrolyte. In the place of sodium chloride all other suitable halide compounds of the alkalis and alkaline earths melting at a red heat can be used as additions.

A.H.W. Aten, H.J. Den Hertog, and L. Westenberg carried out a series of experiments with fused electrolytes in order to determine the nature of the electra deposited metal, when such metal is deposited in solid form (22.) While they studied several metals, e.g. silver, copper, nickel, etc., in detail, they only made a few qualitative tests with manganese, enough to indicate that it was deposited in beautiful crystals. They also noted that a higher current density had to be used for the deposition of manganese than for the other metals studied.

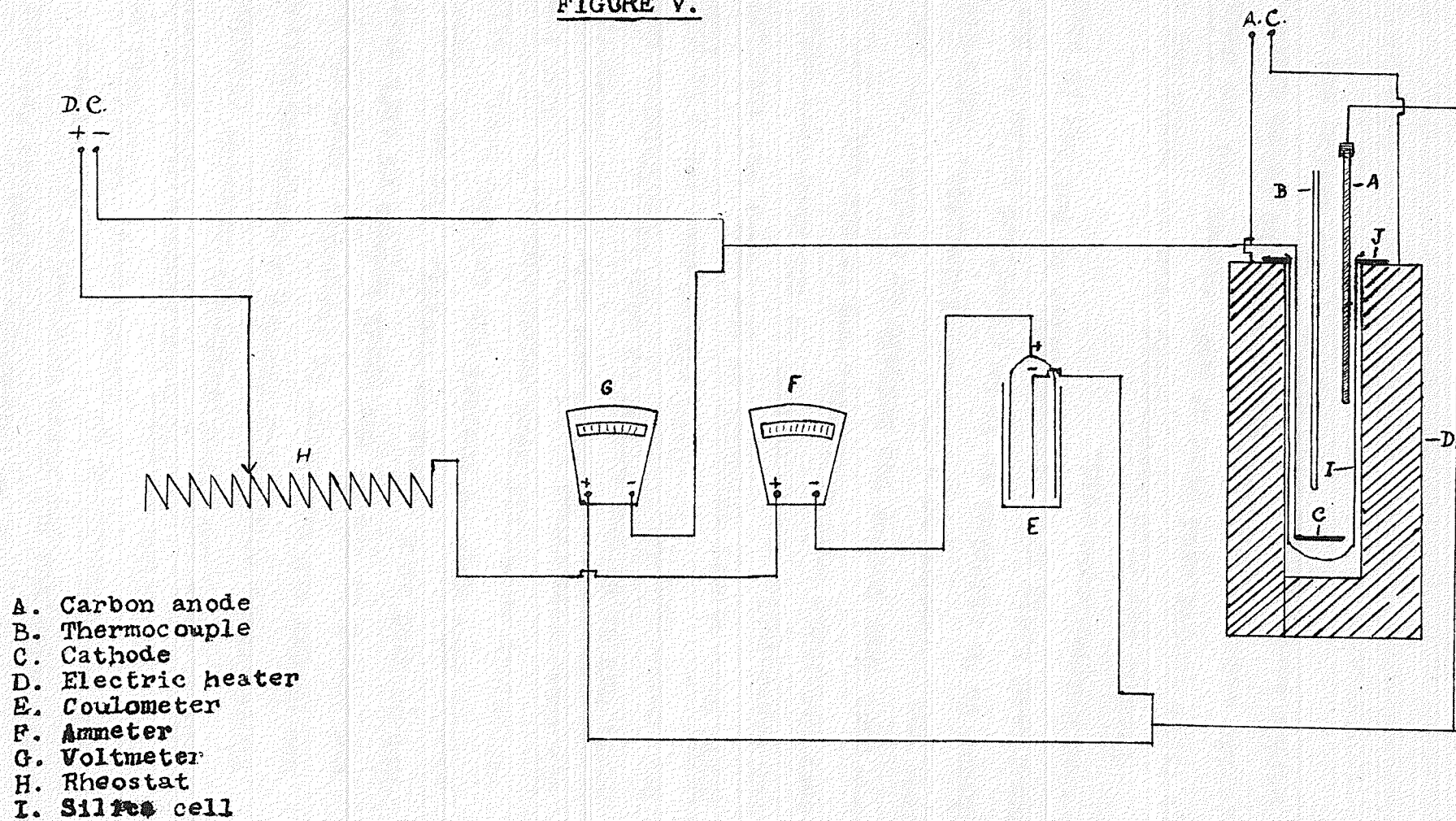
From the above, which was all that could be found in the literature about the electrolysis of the fused salts of manganese, it is evident that, so far, a systematic study of the effects that variations of current density, temperature, and time, have on the current efficiency of deposition and purity of manganese deposited from its fused salts, has not been made. Therefore, it was decided to make a systematic study of the effects that variations of current density, temperature, and time, have on the current efficiency of deposition and purity of manganese deposited from its fused salts.

(3) Experimental.

Ordinary C.P. manganese chloride was used as the electrolyte. This was dehydrated by heating in a stream of dry air at a temperature of approximately 70 degrees centigrade. The resulting anhydrous salt was pink in color and melted quietly. When melted in air, a crust of manganese dioxide was rapidly formed on the surface, but this could be eliminated to a large extent by melting in a current of carbon dioxide. It was only necessary to use a current of carbon dioxide until the electrolysis was started, because, after that, the chlorine evolved at the anode protected the surface.

The electrolytic cell used consisted of a cylindrical vessel 16 centimetres in height, and 1.9 centimetres in width. This was heated in a small electrical resistance furnace. The cathode consisted of stout platinum foil 1.2 square centimetres in area. The platinum lead was protected from the electrolyte by a narrow tube of refractory material shrunk around the platinum but not fused on to it. The anode was a carbon rod 0.75 centimetres in diameter. It was placed at a distance of approximately 5 centimetres about the cathode. The temperature was read by means of a thermocouple immersed in the melt. The appearance of the cell is shown in figure V. The current was kept constant by means of a rheostat and voltage was read from time to time. The current efficiency was determined with reference to a copper coulometer in series.

FIGURE V.



The choice of refractory materials from which the cell was built, was the first difficulty encountered. The first cell used consisted of pyrex glass. This cell withstood the temperature at which the first series of runs were made (660 C.) but the fused manganese chloride attacked the pyrex glass badly, apparently forming a manganese silicate which was opaque and dissolved in the melt. When the temperature was raised to 700 C. the pyrex became so soft that it could not be used as a retaining vessel. The same applied to the narrow tube used to protect the cathode lead. Cells of other refractory materials were tried such as Cornish crucibles, but these were found to be not only badly eaten away by the melt, but to be too porous at high temperatures to retain it. Cells made from fused silica were the ones finally used. These were slowly attacked by the melt, but this effect was not appreciable when compared to the rate that other refractory materials were attacked, and it was only after repeated use that they became too brittle to handle. The platinum lead was protected by a tube of silimanite. This did not appear to be attacked or to be dissolved while in the melt, but flaked badly when cleaned later by boiling in concentrated hydrochloric acid.

Trouble was also encountered with the anode and cathode. The first anodes used were of soft carbon and the manganese chloride attacked them badly, causing the fused electrolyte to become contaminated with carbon. The action was so rapid

that several times the carbon rod broke off before the end of the run. This was largely overcome by using anodes of very hard carbon. The platinum cathode gave trouble by becoming very brittle. After a few runs the platinum became so brittle that sometimes it broke off if moved while in the melt, thus ruining a determination. This brittleness may have been caused by the action of the manganese or manganese chloride, but was more likely due to the action of the carbon, from the anode, in the melt. It was noticed that, after the hard carbon anodes were used, the platinum lasted much longer before it became brittle enough to fracture.

For the first half hour that the current was passed a hissing crackling sound was heard coming from the cell. On looking at the surface of the molten electrolyte many small sparks were noticed. These sparks seem to pass not only from the anode to the electrolyte, but from the anode to the retaining walls, the walls to the fused melt, or the walls to the thermocouple. This utter disregard of where the flash occurred showed that the phenomena was not due to the anode effect, because in that case all sparks would have passed between the anode and the fused melt. It was thought that the sound and the sparks were due to explosions of hydrogen and oxygen liberated by the electrolysis of the traces of water combined with the manganese chloride. At the end of the first half hour this effect passed away.

When a current density of 100 amperes per square



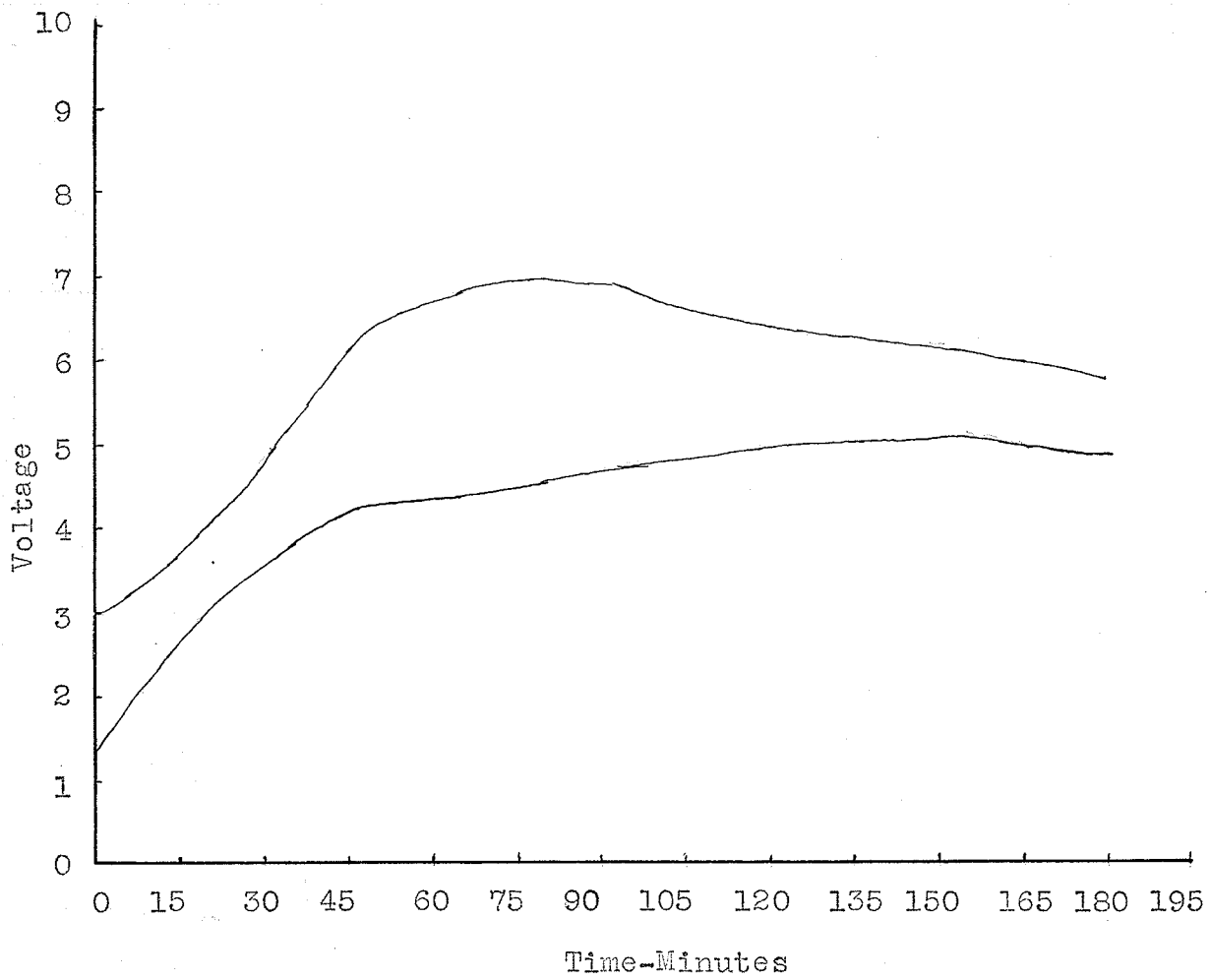
decimetre was used the above effect appeared to be accompanied by a large overheating near the anode, and even when the external heat was lowered, the temperature of the whole melt was raised 50 or 60 degrees centigrade. This effect also passed away at the end of a half hour and after that it was easy to keep the temperature constant at the required point.

The variation of the voltage over a period of three hours was found to follow a general trend in all runs made. It started at a low point and then gradually increased to a maximum and finally started to fall off. The voltage curves obtained at the same current densities and temperatures were not identical, due to the fact that the distance between the cathode and anode was not always the same, thus introducing a variation in the resistance of the electrolyte. Figure VI shows two typical examples of the type of curve obtained from voltage variations.

Several times during runs at 100 amperes per square decimetre, the rheostat commenced to hum, the voltage jumped suddenly, and sparks appeared at the anode, indicating that the "anode effect" was taking place.

The cathode was removed from the melt at the end of three hours and placed in an atmosphere of carbon dioxide to prevent oxidation of the manganese until washed.

Due to the nature of the manganese, which was deposited in large, fragile, feathery crystals or crystalline



growths which extended for approximately 1.5 centimetres above the cathode and were easily broken off by movement of the cathode, a large quantity of manganese was left in the fused melt and had to be separated from it. Equipment was not available for separating the manganese from the melt by screening or pressing, therefore, it was necessary to separate it by washing.

This was attempted at first by allowing the melt to solidify and then washing it out of the tube with water. Hot and cold water were tried, but in both cases it attacked the deposited manganese so rapidly that this method had to be rejected. Ninety-five percent alcohol was tried next, and while this did not appear to attack the manganese, or if it did, to attack it very slowly, it only dissolved the manganese chloride slowly, making the cleaning of the silica tube a long and laborious procedure. The method finally adopted was to remove the cathode, keep it in an atmosphere of carbon dioxide until cool and then wash it off with ninety-five percent alcohol. The fused melt was poured into a large conical shaped iron pan from which the mass could easily be removed when cool. After the melt had solidified it was pulverized in a mortar and dissolved in alcohol. It was found that a large amount of the deposited manganese adhered to the wall of the silica tube after it was emptied. This had to be protected by a current of carbon dioxide while the tube cooled, after which the

electrolyte remaining in the tube was dissolved in alcohol and the manganese adhering to the wall was dissolved in very dilute hydrochloric acid.

While washing the manganese free from the electrolyte it was found that a large quantity of manganous hydroxide was formed. As it was not certain whether or not this was formed by the action of the solvent on the manganese, although this did not appear to be the case, or whether from oxides formed in the electrolyte during the electrolysis, it was decided to make a series of runs and include the manganous hydroxide with the manganese when determining the current efficiency of the deposition. As these determinations gave current efficiency values much greater than one hundred percent it was obvious that the manganous hydroxide must come from the action of the solvent on oxides in the electrolyte.

The method used to test for current efficiencies, at this time, was to dissolve the manganese and the manganous hydroxide in dilute hydrochloric acid, make up to standard volume and analyse an aliquot part for manganese.

The next difficulty encountered was to separate the manganese and manganous hydroxide. It was not possible to wash or float the hydroxide away, because, owing to its large flaky nature, particles of manganese adhered to it and were washed away with it. Therefore, it became necessary to find a solvent which would dissolve the manganese

without affecting the manganous hydroxide, or one which would dissolve the manganous hydroxide without affecting the manganese. Very dilute solutions of hydrochloric acid were tried, but they dissolved one as rapidly as the other. One percent and one-tenth of one percent solutions of acetic acid were used, but these solutions also, dissolved both the manganese and manganous hydroxide. A solution of boiling concentrated ammonium chloride was tried. This dissolved the manganous hydroxide readily, but due to its large dissociation the liquor was slightly acid and therefore, it had a small effect on the manganese. This objection was overcome by adding a few drops of weak ammonium hydroxide.

When the manganese was obtained free, from the electrolyte and manganous hydroxide, it was tested for purity by the evolution of hydrogen from a weighed portion of manganese in a nitrometer. The results from these tests, showing a purity of from 98.5 percent to 99.5 percent, indicate that by this method very pure manganese can be prepared.

During the course of this work many electrolytic runs were made with current densities varying from one ampere per square decimeter to one hundred amperes per square decimeter, and while no figures were obtained for the current efficiencies, it was obvious, from the amounts of manganese deposited, that the current efficiency was much greater at high current densities than at low current densities. At current densities below ten amperes per square decimeter the amount of

deposited during a three hour run was very small, varying from a trace at one ampere per square decimeter to a very small amount at ten amperes per square decimeter. At current densities of 25, 50, 75, and 100 amperes per square decimeter, the amount of manganese deposited was much greater proportionately than the increase in current density.

Runs were attempted at different temperatures from 658 degrees centigrade up to 750 degrees centigrade. It was found impossible to complete a run at 658 degrees centigrade because at this temperature the amperage did not remain constant, but continually varied. The electrolyte seemed to freeze at the top and to prevent easy escape of the evolved chlorine, which escaped spasmodically and seemed to cause the amperage to vary. The lowest temperature at which a satisfactory run could be accomplished was 670 degrees centigrade, and even at this temperature freezing of the melt at the top occasionally occurred. The majority of the runs made were at 700 degrees centigrade. At this temperature no signs of sudden increase or decrease of the conductance of the melt were noted, and a steady current density was easily maintained. Attempts were also made to complete runs at 750 degrees centigrade, but at this temperature, in every case, the fused melt passed through the retaining silica tube before the end of the experiment. The melt did not appear to eat the silica tube and cause a hole to appear, but apparently, either, vaporized and passed through the tube

as a vapour, or else, the silica at that temperature became sufficiently porous to allow the fused melt to pass through it. The manganese chloride of course, changed to manganese dioxide as soon as it was exposed to the air at 750 degrees centigrade. This black deposit of manganese dioxide not only appeared on the outside of the silica tube, but all through the retaining walls. When one of the tubes, in which the above had occurred, was broken, it was found to be black throughout the wall.

Due to lack of time to complete the problem, the work had to be abandoned at this stage.

4. Summary.



While the problem was not completed, and the desired results were not recorded, the above work has cleared away the experimental difficulties encountered, and has established a satisfactory method for obtaining the desired figures.

This method can be summarized as follows:-

- (1). Use a silica tube as the electrolytic cell for all temperatures below 720 degrees centigrade.
- (2). Protect the surface of the electrolyte with a current of carbon dioxide until the electrolysis is started.
- (3). Use as hard a carbon anode as it is possible to obtain.
- (4). After removing the cathode, protect it with a current of carbon dioxide until it is cleaned.
- (5). Pour the fused electrolyte from the silica tube into a conically shaped iron pan and allow it to solidify there.
- (6). Protect the manganese, adhering to the walls of the silica tube, with a current of carbon dioxide, until the tube is cleaned.
- (7). Separate the electrolyte and the manganese by dissolving the electrolyte in ninety-five percent alcohol.
- (8). Separate the manganese and manganous hydroxide by dissolving the manganous hydroxide in a boiling solution of concentrated ammonium chloride, to which a few drops of dilute ammonium hydroxide has been added.
- (9). Determine the purity of the deposited manganese by collecting the hydrogen, evolved from a weighed portion of it, in

a nitrometer.

(10). Determine the current efficiency of the manganese deposition with reference to a copper coulometer by dissolving the manganese in dilute hydrochloric acid and analyzing an aliquot part for manganese.

During the course of the above work, it appeared to the writer, that better results could be obtained if, firstly-- a larger cell was used, so that one could work with larger quantities, and secondly-- if the design of the cell was changed and an H shaped cell, where the anode and the cathode would be in separate compartments joined by a tube at the center, was used. This type of cell would possibly eliminate the trouble caused at the cathode by carbon from the anode.

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