====Light Metals==== From *Extractive Metallurgy of Aluminum 1963*, Gary Gerard, P.T. Stroup, Editors =

Processes Occurring in the Carbon Lining of an Aluminum Reduction Cell

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Abstract

The processes leading to the disruption and failure of the carbon lining of a reduction cell are reviewed with the aim of specifying the properties required in the carbon materials. The reactions with the carbon of the three agents (a) electrolytically liberated sodium, (b) molten electrolyte, and (c) molten metal are considered and their long-term effects as well as their relative importance throughout the various stages of cell life are considered. This leads to a discussion of such properties as thermal conductivity, permeability, pore size, freedom from cracking, and nature of raw materials as well as the more usually measured porosity, electrical conductivity, and strength. Some observations during the examination of failed cathodes are presented.

Introduction

The aim of this paper is to review the various processes occurring during the various stages throughout the life of the carbon lining of a reduction furnace in order to reach conclusions on the qualities required in the carbon lining.

It seems logical to assume that a carbon lining requires: (a) good electrical conductivity, (b) high density or low porosity, and (c) high strength, normally measured as crushing strength.

There are other less obvious qualities to be considered and even those assumed above may require qualification on further consideration.

The active agents which the carbon has to resist would seem to be: (a) electrolytically liberated sodium, (b) molten electrolyte, and (c) molten metal.

Sodium

Sodium is codeposited with aluminum at an activity in equilibrium with the molten aluminum as a function of electrolyte composition at the cathode surface and temperature. The effect of electrolyte composi-
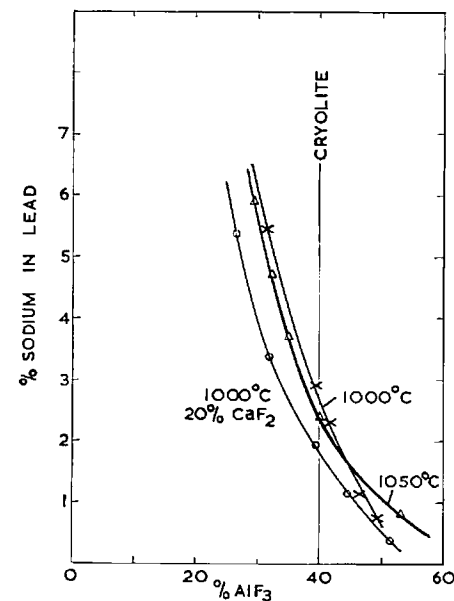

Fig. 1. Variation with electrolyte composition of the sodium content of lead in equilibrium with molten aluminum and electrolyte at 1000 and 1050°C. (In plotting the composition for the electrolytes containing calcium fluoride, the compositions have been calculated on a calcium fluoride-free basis.)

tion on the activity of the sodium at any given temperature can be followed by determining the amount in solution in the aluminum at equilibrium. Because the solubility is low, the percentages are small and not easily determined with accuracy. It is more convenient to determine the amount dissolved in a separate phase of molten lead also in equilibrium with the aluminum (because the solubility in lead is much higher). Figure 1 shows curves for the sodium content of lead, and Figure 2 shows a corresponding curve for sodium in aluminum, but with a greater scatter of the individual measurements. Alumina additions, up to saturation of the cryolite, have practically no effect on the equilibrium sodium contents. Calcium fluoride, as indicated by the curves in Figure 1, seems to have a diluent effect on the equilibrium reaction which determines the sodium content

$$Al + 3NaF \rightleftharpoons 3Na + AlF_3$$
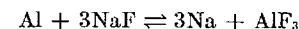
and roughly to the extent which might be expected. Magnesium fluoride would be expected to have a similar effect. Figure 3 shows the effect of

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temperature on the sodium content of aluminum in equilibrium with molten cryolite, but this does not indicate the effect of temperature on the activity of the sodium in the equilibrium because of the change of solubility and vapor pressure of sodium with temperature, etc.; still less does it tell us anything about the effect of temperature on the reaction of sodium with carbon. There is evidence from the "sodium-disruption" type of test of cathode carbons that the reaction increases with decreasing temperature.[1]
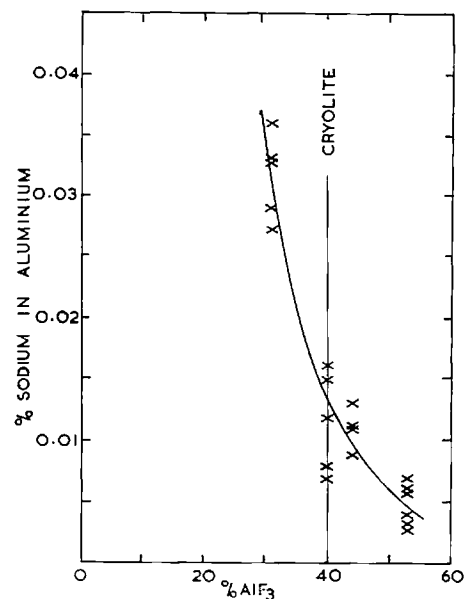

Fig. 2. Variation of the sodium content of aluminum in equilibrium with sodium fluoride-aluminum fluoride melts at 1000°C.

How does the sodium act on the carbon? If one electrolyzes directly on a carbon cathode, sodium can diffuse through the carbon as a vapor, and combine with the carbon apparently as a lamellar compound[2,3] causing expansion. That sodium can behave in this way can be shown by putting a lead-sodium alloy (say, 6% Na) in a graphite crucible fitted inside another crucible made of carbon materials such as are used in lining an aluminum reduction cell. On heating the assembly at 950°C the sodium vapor diffuses through the graphite, without disrupting it because of its superior resistance, yet attacks the carbon crucible outside causing growth distortion and disruption in a matter of minutes. It is
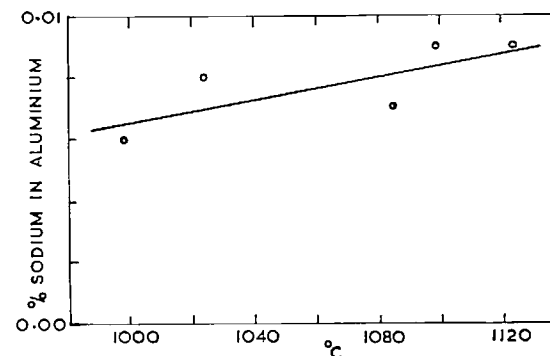
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Fig. 3. Variation with temperature of sodium content of aluminum in equilibrium with molten cryolite.

not necessary for the sodium vapor to condense at temperatures below its boiling point. Similar disruption of the outer carbon crucible can be produced by electrolyzing cryolite in the graphite crucible, but a longer time (3 hr) may be required before shattering occurs, and this takes place without signs of penetration of molten salts.

Various cathodic-disruption tests have been devised based on this sodium attack.[1,4] In these the carbon test sample is made cathodic in a melt of cryolite with various additions; in some, potassium salts are added to accelerate the disruption. (Potassium behaves like sodium but the larger atom is more disruptive.) Such tests are useful in assessing the suitability of raw materials for cathode construction, and to a limited extent in testing the finished product; but they measure resistance to only one form of attack and can therefore be misleading if one attempts to use them as a final criterion of cathode quality.

Such tests carried out by the writer in 1936 placed raw materials in the following order of increasing resistance to attack—metallurgical coke, pitch and oil cokes, anthracite, graphite. This is different from the order given by Panebianco and Bacchiega[1] (i.e., petroleum coke, metallurgical coke, anthracite, graphite), and the difference may be due to origin and therefore type, and perhaps also purity, of some of the carbons.

Molten Electrolyte

Electrolyte by itself and while remaining molten has practically no effect on cathode carbon, but it can soak through the carbon and freeze or crystallize and by so doing disrupt and heave the carbon lining. The

factors involved are worth further consideration although they are not yet fully understood.

The electrolyte penetrates the carbon much more readily after the latter has been made cathodic. It may be that carbon which has been attacked by electrolytically liberated sodium, with the formation of the carbon-sodium lamellar compound, is then more easily wetted by molten electrolyte.

There is no real evidence that any particular constituent of the electrolyte is absorbed preferentially. Compositions found in the cathode can be explained by the prior penetration of sodium and its subsequent reaction with mixed fluorides of the normal bath composition. Normally, therefore, a salt mixture containing excess sodium fluoride is found in the lining. These processes are sufficient to explain the preferential loss of sodium fluoride from the bath in early life, a loss which gradually decreases with increasing age of the lining so that it is later outweighed by the loss of fluorine at the anode and bath surface, which loss is in effect equivalent to a loss of aluminum fluoride.

The surface tension of the molten electrolyte increases with decreasing temperature so that the electrolyte is sucked or drawn through the capillaries of the lining down the temperature gradient. This movement down a temperature gradient can be demonstrated by a very simple experiment with a drop of the molten electrolyte on a platinum wire in which a temperature gradient can be produced. The drop will move down the temperature gradient, even against gravity, due to the difference in temperature between the two ends of the drop. There are therefore two forces assisting the penetration, the hydrostatic head of the bath and the capillary attraction down the temperature gradient through the lining.

When the salt mixture reaches the isotherm corresponding to its liquidus, some constituent will freeze or crystallize. According to observation, columnar crystals are produced growing at right angles to the isothermal surface, and the crystal growth forces are apparently sufficient to cause opening up of the carbon and the characteristic layering or stratification. The whole process of movement down a temperature gradient, freezing at a particular isotherm with the formation of columnar crystals causing an expansion perpendicular to the isothermal plane and stratification and layering of the carbon is analogous to the "frost heave" which occurs beneath cold storage buildings or near the surface of the ground in cold weather. In the latter case, moisture can be drawn upward against the force of gravity to the 0°C isotherm where it freezes as columnar crystals whose growth can produce tremendous forces, at right angles to the 0°C isotherm, capable of lifting buildings. Character-

istic layered structures or lenses of ice crystals are often produced.[5] Similar layered structures or lenses of columnar crystals are found in reduction furnace cathodes (see Fig. 4).

The phenomenon of frost heave in water systems has been studied by several investigators, and their observations on factors influencing frost heave may be pertinent when considering carbon cathodes.

According to Taber,[5] "Growth of ice crystals under resisting pressure in open systems is analogous to the growth of crystals from solutions under similar conditions. One is possible because water occupying
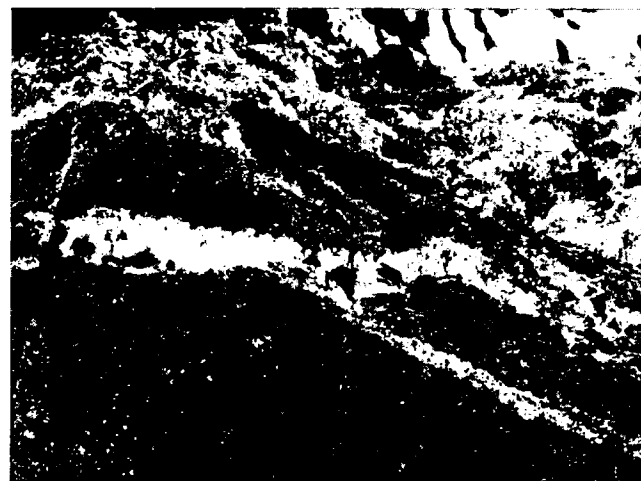

Fig. 4. Photograph of portion of cathode showing layered structure and columnar crystals of frost heave zone.

very small voids can be supercooled; the other because solutions in such voids can be supersaturated." Freezing in porous media, with the formation of ice lenses and the development of frost heave, has also been discussed by Jackson and Chalmers.[6]

In cathodes we have crystallization from solutions, as the liquid electrolyte penetrates the carbon until it reaches the isotherm of the liquidus temperature when the primary constituent crystallizes; the mother liquor or liquid phase may continue downward to the isotherm of another arrest point where another crystal phase may separate. Because we have a complex solution there may be several isotherms at which frost heave may occur simultaneously.

Crystals such as those shown in Figure 4 were found to be practically pure cryolite: 97.7% cryolite, 0.4% AlF_3, 1.2% Al_2O_3, and 0.7% CaF_2.
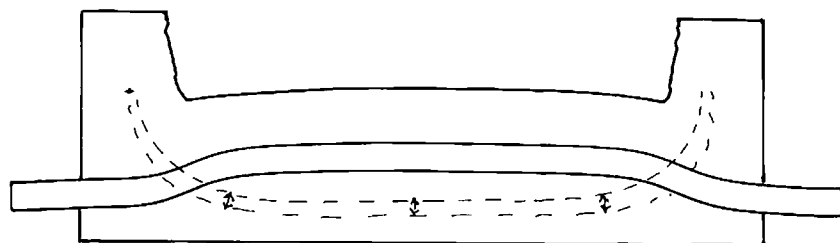
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Fig. 5. Distortion produced by frost heave (diagrammatic).

On other occasions similar columnar crystals have been found to be practically pure sodium fluoride, or to correspond very closely to the cryolite-sodium fluoride eutectic. These must have crystallized from a complex solution.

What is the temperature range over which this frost heave can occur? The penetrating liquid will inevitably be saturated with alumina and contain some calcium fluoride and probably sodium fluoride. The cryolite might therefore begin to crystallize out somewhere below, say, 940°C. (Observations on cathodes during dismantling suggest that this is placing the upper temperature limit rather high.) Some liquid phase will probably continue to penetrate down to the sodium fluoride-calcium fluoride-cryolite eutectic at 785°C or probably lower because of other impurities picked up on the way. Although large α-alumina crystals are found, the writer has seen no evidence that alumina forms crystals of the frost heave type.

It should be noted that the forces developed are directional, not merely upward because of less resistance to expansion, but perpendicular to the isotherm and in the direction of growth of the crystals. In the cathode of a reduction cell the isotherms might be described as saucer-shaped. The frost heave zone therefore leads to a type of distortion shown diagrammatically in Figure 5. Where the zone crosses the steel conductor bars, a bending of the bar into the shape of a crank is observed. The distortion and disruption are complicated by the fact that the zone passes through different materials having different strengths and, no doubt, different frost heave characteristics. It is believed that this freezing zone is responsible for the major part of the growth and expansion of a cell lining during life, and primarily responsible for the arching of the cathode and bending of the conductor bars.

In the case of frost heave by ice formation, it has been observed that some soils are more susceptible than others; a fine pore size is apparently necessary. According to Casagrande,[7] for example, "Under natural freezing conditions and with sufficient water supply, one should expect considerable ice segregation in non-uniform soils containing more than three per cent of grains smaller than 0.02 mm, and in very uniform soils containing more than ten per cent smaller than 0.02 mm. No ice segregation was observed in soils containing less than one per cent of grains smaller than 0.02 mm, even if the ground water level was as high."

Observations on frost heaving beneath cold-storage buildings have confirmed the criteria put forward by Casagrande. It is very probable that corresponding criteria apply in the case of frost heave by crystallization of constituents of the electrolyte in cathodes of reduction cells, but as yet these cannot be stated. It may be that we should avoid a fine pore size in the carbon lining, but at the same time a low permeability may be of value. It is interesting to note that Ulm, in discussing the paper by Panebianco and Bacchiega, stressed the importance of mechanical structure and grain size in carbon cathodes but gave other reasons than those above. He stated that the grain size should be as coarse as possible so that sufficient mechanical strength is given, that the coarse grain would offer a smaller surface for chemical reaction, and that the porosity should be sufficient to permit an "internal growing" of the blocks. In the author's experience, blocks of low permeability have given the best results.

It should also be noted that this frost heave is not a question of alternate freezing and thawing but develops under steady state conditions. Alternate freezing and thawing may introduce complicating factors and accelerate failure, and for this reason temperature fluctuations within the lining should be avoided.

During the life of the cathode the isotherms with which we are concerned must move downward, for saturation of the carbon with electrolyte must increase its thermal conductivity without improving the electrical conductivity correspondingly. Also, as will be pointed out later, graphitization of the carbon occurs, and graphite has a much higher thermal conductivity. The thermal insulating layers below the carbon will gradually be destroyed by penetrating electrolyte. Not only is there a zone of temperature for frost heave conditions but also that zone moves during life so that a whole family of frost heave layers might be expected to be visible in a cathode during dismantling. On the other hand, a layer once started probably has a self-stabilizing action due to its relatively low thermal conductivity.

Penetration of the lining by electrolyte is not uniform. In a cathode built of prebaked blocks, penetration occurs much more readily along the joints than into the body of the blocks, although some penetration

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into the latter may occur along cracks which inevitably seem to be present. Liquid penetration may never reach the center of some blocks, as will be seen later. Similarly, in rammed monolithic cathodes, penetration probably occurs preferentially along cracks. All this leads to a non-uniformity in the processes occurring.

In frost heave the growth often starts at a discontinuity already present, the surface of a pebble or stone, probably starting there when the 0°C isotherm was spreading downward through the ground after the onset of the frost. Similarly in a cell lining we might expect the heave to begin at a discontinuity already present, for example, the upper surface of the conductor bars.

If penetration of the carbon by electrolyte cannot be prevented, then it is desirable to ensure that (a) whatever frost heave occurs takes place in a relatively harmless position, in particular, (b) the carbon cathode is not lifted off the conductor bars and, if possible, (c) the effective cathode is lifted as a whole. If frost heave occurs above the conductor bars, the electrical connection is seriously impaired and other effects follow. The frost heave zone should therefore be below the carbon over the whole area of active cathode, and it is most important to ensure that this is so during the early stages of life. It is therefore necessary to consider the amount of thermal insulation below the cathode, particularly toward the ends where colder conditions obtain and where the frost heave zone is likely to rise into the carbon, causing separation of the carbon from the conductor bars.

There is therefore a certain minimum amount of thermal insulation which must be used below conductor bar level. Moreover this minimum amount will vary with the thermal conductivity of the carbon lining. The lower the thermal conductivity of the carbon, the greater must be this minimum amount of insulation.

Another point to note is that a cell design appropriate for a given carbon lining material may not be appropriate for another carbon, although the latter may give very good results elsewhere in an appropriate design of cell. Carbon cathode qualities therefore should not be considered apart from design of the cell in which it is to be used.

The thermal conductivities of carbon materials at the temperatures in which we are interested are not easy to measure and really adequate information is not available.

More information is undoubtedly required on these frost heave phenomena, on the fundamental principles involved, and on the relative behavior of different materials. But it is not easy to develop a simple test and, as far as the author is aware, none has been suggested.

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Molten Metal

Penetration of the carbon by molten metal is perhaps a simpler process, but ultimately more disastrous. Some aspects of metal penetration are worth further consideration.

Ultimate failure usually occurs by metal penetration to the steel conductor bars, leading to iron pickup, local concentrations of current, and therefore heat, and perhaps final run-out. There is evidence that some metal penetration of the carbon lining usually occurs in very early life, perhaps even in the first few days, yet the cell may have a normal life. What determines whether the metal penetration will be progressive?

Aluminum in contact with carbon at the temperatures of the carbon lining, and in the presence of flux, forms aluminum carbide at the interface. The examination of a cathode during dismantling suggests that small veins of aluminum in the carbon may be partially or wholly converted into carbide, while in larger veins the carbon surface has the appearance of having been washed or corroded away by the aluminum.

If a metal vein is so located that it tends to carry current, then, no doubt, under the action of the magnetic fields some circulation of the aluminum will be set up. The rate at which iron contamination can reach the metal pool in the cell from the conductor bars and through veins of surprisingly small cross section suggests that the circulation may be quite rapid. It would seem that such circulation may wash out the carbide as it is formed, keep the vein open, and gradually enlarge it.

It is suggested therefore that there may be a certain critical size of vein below which the vein may be self-sealing by the formation of aluminum carbide, but that larger veins where there is circulation may gradually grow by attack or erosion of the carbon walls.

This self-sealing can perhaps be helped by partially or wholly blocking the hole by applying relatively coarse and highly crystallized, and therefore relatively insoluble, alumina to the surface of the cathode of an operating cell when iron pickup occurs.

It is therefore important to avoid any rapid cracking or opening-up of the carbon cathode. If expansion and distortion occur slowly, the self-sealing effects may take care of it.

Some Observations on a Sample of Used Cathode Block

At this stage, and before considering the interaction between the three disruptive processes described above, it is illuminating to consider a sample of a prebaked cathode block taken from a cell which failed after a short life. A cut section of this block is shown photographically

Fig. 6. Cut section of used cathode block showing coring.

in Figure 6, while Figure 7 shows diagrammatically the position of the sample with respect to the original block mounted on its conductor bar. The section shows a cored structure. In the photograph the central core appears as a darker area. This area appeared to be of a similar nature to the unused block material, but on analysis contained about 6% sodium yet very little fluorides. (The interaction of this alkali with atmospheric water produced the white efflorescence seen in the photograph of the cut section.) It would therefore appear that this area has been permeated by sodium diffusing from the cathode surface, but has not at this stage been penetrated by liquid electrolyte. Outside this area and with a sharp demarcation line there is an area which appears lighter in the photograph because it has been graphitized and has therefore become polished in the cutting operation. Analysis, or alternatively ashing, of a thin cross-sectional sample showed that this area has also been fully penetrated by liquid electrolyte and the composition of this electrolyte is roughly equivalent to a combination of the electrolyte in the normal bath with the sodium which has previously penetrated into the carbon. The frontier of electrolyte penetration is quite sharp and corresponds to the boundary seen in the photograph.

The graphitization of the carbon was confirmed by x-ray examination. In cells of longer life, complete graphitization of the whole block occurs. It is difficult to understand how graphitization takes place at temperatures of the order of 900–1000°C, yet this must happen, for it is a general

effect not confined to isolated areas and there has been no reason to believe that the cathode has been overheated. It would seem that the carbon is first converted into the lamellar compound by the penetrating sodium vapor, and that later when liquid electrolyte reaches this compound it is decomposed with the formation of graphitic material.

The electrolyte penetration has not occurred uniformly from the upper surface but has obviously penetrated preferentially along the joints between the blocks and along cracks within the blocks, soaking inward from these surfaces, as revealed by the pattern of the center part. It is interesting to note that there are also cracks apparently following the
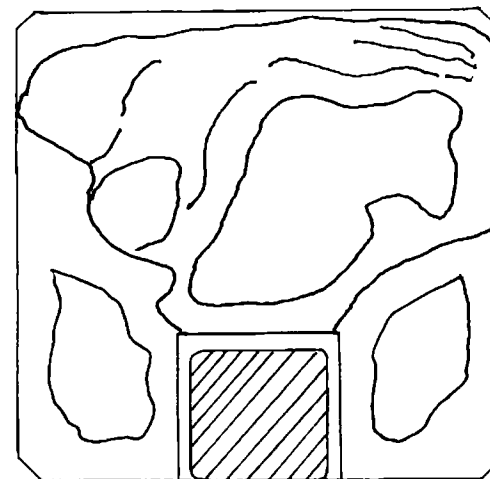

Fig. 7. Diagram showing position with respect to original block of portion shown in Fig. 6.

present boundary of the central core and also corresponding perhaps to earlier positions of this boundary. This may suggest that the graphitization is accompanied by some volume change or, alternatively, that the central core and outer graphitized regions have different coefficients of thermal expansion and that the cracks have developed in cooling after shutting down the cell. Once the block has been fully penetrated by electrolyte and graphitized, it appears to be relatively inert and probably resistant to any further attack by alkali metal.

From the appearance of the cracking in this section it is easy to realize how the flaking-off of the upper surface might occur; such flaking is sometimes observed in cell operation during early life.

Combination and Interaction of Disruptive Processes

The expansion caused by sodium attack is nondirectional, i.e., it is probably uniform in all directions and might not therefore be expected to lead to disruption. On the other hand it may occur from the top surface downward as the penetration spreads through the cathode. A rapid production of sodium in early life might cause flaking-off of the surface, but if the attack can be kept slow it may lead to little more than a small general expansion which of itself may not be very harmful, in fact it might help by tending to close up any cracks.

The form of the expansion curves presented by Rapoport and Samoilenko[4] suggests that under alkali metal attack the best materials may quite quickly expand by something of the order of $2^1/_2\%$ linear expansion and show no further expansion. In the test by these workers the maximum expansion was reached in about 2 hr. There is no evidence that the carbon lining goes on expanding at this rate, and indeed final expansions during the life of a cell cannot be much more than that observed in this 2-hr test.

The sample described in the previous section suggests that the lining may become inert to any further alkali metal attack. It is doubtful, therefore, whether alkali metal attack is of much significance in determining the ultimate life of a cell provided that (a) reasonably good raw materials, according to the alkali metal test, are used in the first place and (b) rapid attack by sodium is avoided in the starting up and very early life of the cell.

The frost heave forces are directional and tend to produce a lifting and arching of the cathode so that cracks may develop permitting metal penetration. If the arching occurs comparatively slowly, and if it tends to lift the whole cathode surface, rather than true arching, then any cracks formed may be sealed as they form. It is the rapid opening of cracks which is to be feared. The final state of a cathode after a long life is often amazing. If one could imagine all the impregnants removed, there would be little more than a loose carbon structure. Apparently some sealing process must occur. If deformation cannot be avoided, it is important that the rate of deformation be slow and steady.

The expansion of the upper surface produced by slow alkali metal attack may in fact help to seal up the cracks which would otherwise be formed by the arching produced by frost heave. Some differential expansion of the upper face of the cathode with respect to the bottom may not therefore be a bad thing.

Since alkali metal attack followed by electrolyte impregnation apparently produces graphitization of the original carbon materials, the argu-ment for using graphite as a component of the lining may have merit. Incorporation of a proportion of graphite in the carbon lining mixture does indeed seem to have beneficial results, whether produced by electrical calcination of the anthracite which forms the major constituent, or whether deliberately added as a proportion of graphite as normally produced from a petroleum coke. Panebianco and Bacchiega[1] recommended 30% of graphite, while, in the discussion on their paper, Ulm doubted whether such a high percentage was necessary to give an effective increase in life of the cell.

In considering the addition of a proportion of graphite and its effects, the effect on the thermal conductivity should be considered, for this may affect the position of the frost heave isotherm and thus have a marked effect on life in one particular cell design.

It is interesting to consider how these effects come into play in the various stages in life of the lining.

Baking

The lining must first be baked or brought up to temperature. Cracks may develop in this process due to shrinkage of the components. Essentially two forms of construction have been used: (a) prebaked block lining, and (b) the rammed monolithic lining.

By the use of blocks which have been prebaked at an adequate temperature (say, 1250°C), so that they will not shrink even on prolonged exposure at the operating temperature of about 950°C, it is possible to ensure that the bulk of the lining will not shrink further. Even such prebaked blocks must be joined, and perhaps surrounded, by some rammed material. To minimize shrinkage of such rammed material surrounding the prebaked blocks, or constituting the entire monolithic rammed lining, the carbon aggregate must be precalcined and fully shrunk. This calcination is also necessary in the aggregate used for the prebaked blocks, if cracking in the prebaking process is to be avoided.

Two methods of calcining the aggregate are used in practice: (1) electrical calcination, usually in vertical shaft furnaces; and (2) gas or oil-fired calcination in rotary furnaces.

The former method is capable of higher temperatures but usually results in a less uniform product. Some of the particles may be fully graphitized while others may be inadequately shrunk. Measurement of the average properties of the product such as real specific gravity and volatile content may not be adequate safeguards, and direct measurement of shrinkage may be necessary.

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Calcination in a rotary furnace, oil or gas fired, produces a more uniform product but usually with a lower average level of calcination and no graphitization. Specific gravity and volatile tests based on experience may give adequate assessments.

Even with a fully shrunk aggregate, shrinkage of a rammed monolithic lining can occur if the binder content is not kept to the absolute minimum. This binder shrinkage can also be measured in a suitable test, say, on a test piece prebaked to 500°C and then taken to and held at 1000°C for a given time.

Starting

After baking or preheating, the carbon lining cannot be regarded as a perfectly uniform material of given properties. It inevitably contains minor defects, cracks or joints, and these must be taken into account in the starting procedure. Starting techniques have varied, particularly according to the stage at which the metal is added. The metal has a lower melting point and a higher specific heat than the electrolyte and consequently, if it gains access to the lining, will tend to flow further than the molten electrolyte before freezing. On some occasions techniques have been used in which the molten metal has been added to the cell first, but for the reasons given above this is undesirable. It is better to add the electrolyte to cause some sealing of the lining by comparatively harmless electrolyte and perhaps also by deposits or sediments of alumina.

There is some value in adding metal soon after the bath has been formed. If cryolite is electrolyzed onto an exposed carbon surface the electrolytically liberated sodium quickly diffuses into the carbon and more is formed. A rapid sodium attack is obtained just as in the laboratory tests mentioned above. A layer of metal acts as a blanket or barrier protecting the carbon. This action is due to the low solubility of sodium in the metal layer. The cathode therefore should be protected by adding the aluminum blanket within a few hours after starting.

The more the sodium attack can be controlled and made more gradual the better. The total final expansion may be the same, but it should be a gradual attack, and in depth, rather than a rapid attack on the surface which can cause flaking.

Early Life

Apart from avoiding rapid sodium attack it is important to ensure that frost heave does not occur at dangerous levels particularly during

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early life. At this stage the carbon cathode is likely to be cooler and has not yet developed the higher thermal conductivity which it will have in later life due to flux impregnation and graphitization. It is therefore important to avoid deposits on the surface of the cathode which may interfere with the current distribution and therefore temperature distribution. Deposits toward the ends of a cathode can be particularly undesirable in that they restrict current flow in this region causing that portion of the cathode to get colder than normal, so that the frost heave isotherms rise to a dangerous level and progressive deterioration of current distribution sets in. The entire cathode should be kept sufficiently hot to be free of deposits at this stage.

Normal Operation

In normal operation the temperature conditions should be kept constant. Operation should be continuous, and any fluctuations in external cooling should be avoided. Artificial cooling by upsetting the isotherms can be particularly disastrous.

If expansions and frost heaving cannot be completely avoided, an attempt should be made to slow the rate, to avoid rapid cracking of the lining, and to enable the self-sealing process to occur. Experience indicates that the expansions should be restricted or directed by strong support to the steel box structure.

Conclusion

It is concluded that the more obvious properties required in the carbon lining material (a) good electrical conductivity, (b) high density or low porosity, and (c) high strength, be extended to include the following.

1. A small total expansion under the action of alkali metal attack. This involves an appropriate choice of raw materials.

2. Good thermal conductivity, or at least a thermal conductivity appropriate to the cell design, so that frost heave isotherms are below conductor bar level.

3. A coarse porosity or at least absence of fine pores (consistent with low porosity as mentioned above and perhaps low permeability) to give low susceptibility to frost heave.

4. The carbon material should contain a proportion of graphite. This seems to be an advantage according to practical experience. It improves the electrical and thermal conductivities and it is logical to start with a material that is ultimately formed anyway.

5. A low permeability is desirable to keep down the rate of electrolyte penetration to the frost heave isotherm. This may be debatable, but in the writer's experience blocks with low permeability have given the best results.

But more important than all these qualities which can be measured on a block or sample of the material is a freedom from defects through which electrolyte and metal can penetrate. Ultimately metal penetration occurs through defects rather than through the bulk of the carbon material.

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Discussion

K. B. McGhee (*National Carbon Co., New York*): Can you give a breakdown as to what is meant by "fine sizes?"

J. Waddington: When considering frost heave in soils, fine material is usually defined as less than 0.02 mm grain size. This is an arbitrary level but might be adopted as an approximate guide for cathode linings. The heaving pressure is inversely proportional to pore size and therefore to particle size.

E. A. Hollingshead (*Aluminium Labs. Ltd., Arvida, Quebec*): The author attributes heaving of the carbon lining to the forces produced by the growth of columnar crystals of cryolite and other fluorides, and points out that it is analogous to the frost heaving of the ground. It might be mentioned that, contrary to popular belief, frost damage has no necessary connection with the expansion which occurs when water freezes. Hence, the analogy is sound even though cryolite shrinks on freezing.

In a recent paper on the thermodynamics of frost damage in porous solids, Everett [D. H. Everett, *Trans. Faraday Soc.*, **57**, 1541 (1961)] relates the heaving pressure to the interfacial tension of ice against water and to the effective radius of the small pores. With his formula the heaving pressure for cryolite freezing in a carbon lining has been calculated to be of the order of 1 kg/sq cm. This is considerably less than the tensile strength of carbon. Could this pressure cause heaving and, if not, does the author believe the crystal growth forces are greater than this?

J. Waddington: In the paper to which Dr. Hollingshead refers, Everett calculated heaving pressures in water systems of 0.1–1 kg/sq cm., acknowledging that there was uncertainty because of the unreliability of the thermodynamic values for water and ice involved in the equation, and pointing out that the pressure varied inversely as the micropore size. Yet frost heave can lift cold-storage buildings. I am not sure what values Dr. Hollingshead has taken for the interfacial tension of molten cryolite

against the solid crystals or for the pore size, but his value seems of the right order; the force would be more than sufficient to lift the weight of the lining and cell contents. It is of the same order as that calculated for water systems where frost heave can lift buildings. As the pressure developed is inversely proportional to pore radius, there will be, for any given mechanical strength, a critical pore size below which frost heave can develop.

The existence on particular isotherms of the columnar crystals, strongly resembling ice lenses, and the features of the distortion associated with these layers seem ample evidence that a similar phenomenon occurs in reduction cell linings.

R. B. Newman (*Reynolds Metals Co., Sheffield, Ala.*): Should frost heave line be kept below the collector bars?

J. Waddington: The frost heave line should be kept below the collector bars, otherwise there is the danger of lifting the carbon from the bars and seriously increasing the electrical resistance of the bottom. This can happen, particularly toward the cooler ends of a cell.

Pierpont (*National Carbon Co.,*): How do you explain cavities filled with 90% molten aluminum?

J. Waddington: It is not easy to explain all the observed features by one theory, but the frost heave phenomenon is a complex one because there are a number of constituents freezing-out from the molten salt mixture and therefore a range of frost heave isotherms; moreover, these probably move downward during the life of the cell as the thermal conductivity changes with penetration, and a crystal lens formed at one stage may afterward melt out and be replaced by metal. Alternatively, the complex geometry of the heaving may open cavities in part of the lining.