

RAMMING PASTE RELATED FAILURES IN CATHODE LININGS

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Some common failures that may be introduced into the rammed parts of cathodes during installation, preheating or early operation are discussed. Most emphasis has been put upon the shrinkage behaviour of ramming pastes during baking and upon crushing of aggregate particles during ramming. Incomplete knowledge of such materials properties may lead to early failure of electrolysis cells.

INTRODUCTION

Modern cathode lining design is a product of high technology as well as thorough understanding of the construction materials that are used, their chemical and thermomechanical properties, and how they interact with each other and with the chemical environment they are exposed to during the normal life-span of the lining. An ideal cathode should be kept operating for the time it takes the normal chemical and mechanical forces to wear it down, *i.e.* 10 years or more. This is, however, most often not the case.

Autopsies have shown that a large number of early failures, *i.e.* pot lives less than 2 - 3 years, are caused by weaknesses in the rammed parts of the lining. The use of ramming paste in the pot has several purposes. Its main purpose is to fill the voids between the prebaked bottom blocks and between the blocks and sidewall materials and thus prevent liquid aluminium and bath from penetrating into the interior of the lining. Another purpose is to provide a layer that is able to absorb some of the thermal expansion of the bottom blocks during cell preheating. Peripheral seams also result from the geometrical problem of fitting the blocks into the potshell if the shell has a permanent deckplate. Ramming of collector bars is an alternative to cast iron sealing.

Two main topics will be addressed in the paper; the failures that are introduced during the ramming operation, and the failures that occur as a result of paste shrinkage during baking.

PASTE COMPACTION

Different philosophies exist with respect to the desired compaction level of the ramming paste, *i.e.* as high as possible or only to a certain degree. The reason for the latter is that a "loose" peripheral seam may act as a compressible zone after baking. It seems, however, more reasonable to include a more defined crushable material somewhere else in the lining [1], and not where liquid aluminium and electrolyte may find their easiest access into the interior of the cathode.

Selection criteria for ramming pastes [2] and green density control during compaction of cold type ramming pastes in cathodes [3] have been reported. It was suggested that the rammed density of joints and seams should be close to the maximum obtainable green density of a given paste but that too much ramming could be equally detrimental to the rammed parts as too little compaction. When a certain degree of compaction is reached, the extra work needed to further increase the green density may rise sharply (Figure 1). Although it may be possible to increase the compaction of a given paste marginally it may not be work effective and, as will be shown in the following, also be detrimental to the baked quality of the paste.

Porosity and density. Open porosity will always constitute a considerable part of the baked paste as well as the prebaked block volume, allowing bath components to percolate through the carbon lining. A proper compaction will, however, considerably reduce the pore volume (Figure 2) and slow bath percolation through the lining in the critical start-up and early life period of the cell. After a few months of cell operation all open porosity in the joints and seams will be filled with bath components, but by that time a natural barrier being formed by slow reactions between bath components and refractory materials should stop or slow down further degradation of the refractory/insulating parts of the lining.

Green density of rammed seams and joints will directly influence the mechanical, thermomechanical and electrical properties of the baked paste. The peripheral seam is usually not designed to transfer electrical current while the bottom block joints should be able to do so. The

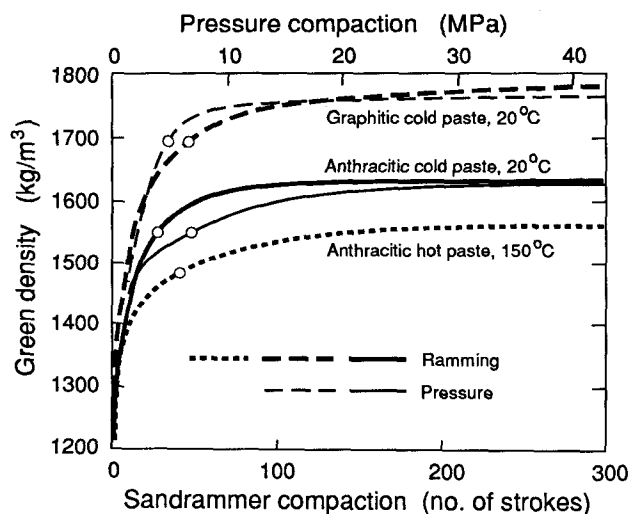


Figure 1. Green density versus compactive work for some cold and hot type ramming pastes (laboratory). Circles indicate 95 % of maximum green density.

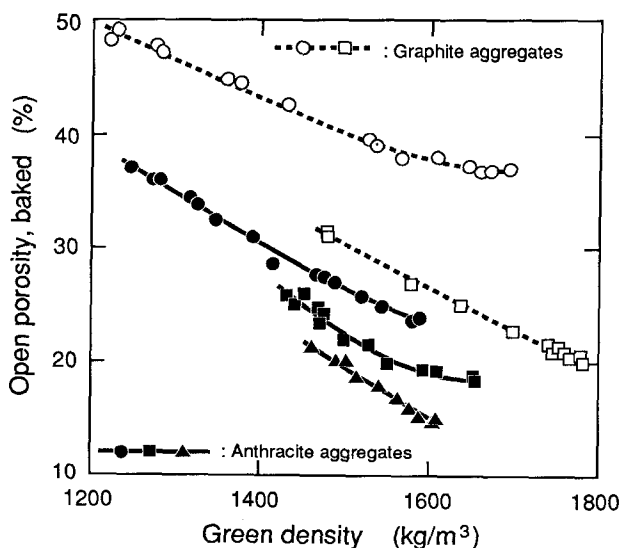


Figure 2. Open porosity (baked) versus green density for some cold type ramming pastes.

latter is especially important in the event that cracks should form in the normal current path between the current collector bars and the cathode carbon surface. The usual situation is, however, that for convenience and inventory reasons only one type of paste is used for both peripheral seam and bottom block joints. It is also obvious that paste used for ramming current collector bars should have as low electrical resistivity as possible (e.g. graphitic aggregate) and be rammed to a density close to its maximum green density (Figure 3).

Electrical resistivity. Electrical resistivity of baked paste will generally decrease with increasing compaction due to an increase in the particle-particle contact area (and binder coke bridges) in the paste. Excessive ramming or

compactive work may, however, lead to crushing of aggregate particles and will, to a greater or lesser extent, take place in most ramming pastes. From the curves in Figure 3 this can be visualized as no change in electrical resistivity or an increase in resistivity values as the green density increases, due to the obstruction of the current path the crack formation will cause. One paste (●) made from electrocalcined anthracite, ECA, is an extreme example, even moderate densification leads to extensive crushing of particles, visualized by the large scattering of experimental electrical resistivity as the density increases (shaded area). According to Belitskus [4] the occurrence of highly crushable particles in ECA lots can seriously degrade cathode seams, and possibly, blocks. The formation of such mechanically weak particles is affected by both raw material and calcination factors.

Mechanical strength. Crushing of aggregate particles during ramming will create new particle surfaces that are not wet by binder and thus unable or difficult to bind properly to the rest of the paste during baking. The size and concentration of these flaws may therefore have a great impact on the mechanical strength of the baked paste. This can readily be shown by measuring the strength of baked carbon specimens made from paste that contains a small fraction of easily crushable particles in the aggregate. Measurements have shown that the mechanical strength of the baked carbon specimens increases fairly linearly with increasing green density for tamping pastes that does not contain, or contain a negligible amount of, easily crushable particles (Figure 4). If, however, particles start to crush during compaction, this linear relationship breaks down at a certain density level. The experimental values scatter, depending on the number of flaws or the size of the critical flaw introduced into the specimen. The shaded areas in Figure 4a,b illustrates in which range this density-strength relationship breaks down. In ramming pastes that contain relatively large amounts of easily crushable particles the sudden and pronounced scatter of experimental points shown in Figure 4 may be obscured as the break-down may start at very low densification levels. The baked paste will tend to

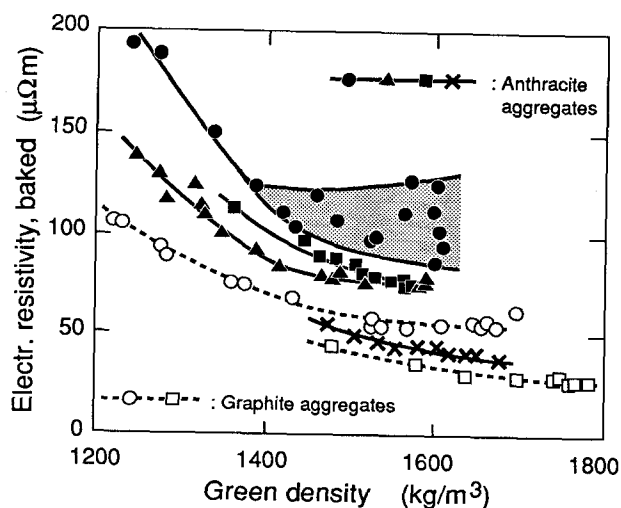


Figure 3. Electrical resistivity versus green density for some types of cold ramming pastes.

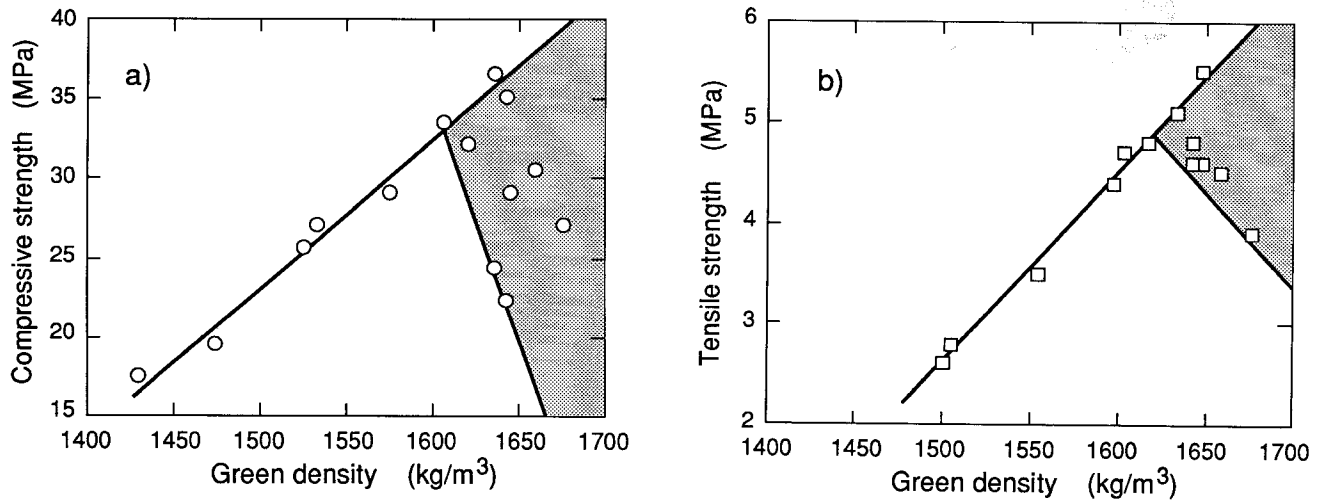


Figure 4. Compressive strength (a) and tensile strength (b) of baked specimens versus green density. Shaded areas illustrate where coarse aggregate particle are being crushed.

appear crumbly having very low mechanical strength throughout the entire density range.

The most extensive damage in terms of particle crushing during ramming of cathodes takes place at or near the paste surface. As the seams and joints necessarily have to be rammed or compacted in layers, the damage caused by over-ramming may degrade the rammed surface to the extent that the next paste layer does not adhere and may easily be peeled off. This leads to stratification of the rammed parts and an increased probability of bath and metal penetration. An example of this, taken from an autopsied cathode, is shown in Figure 5. The paste had been densified by means of a too high compaction pressure using a mechanical type compaction equipment. The stratification failure in the peripheral seam, displaying the grooved "roller" imprint, can be seen in the photograph.

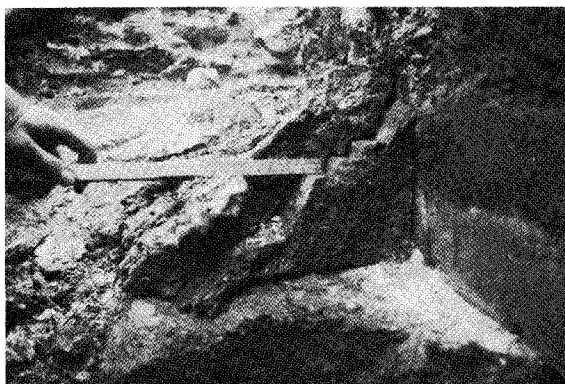


Figure 5. Photograph from autopsied cathode shows stratification and lack of bond formation between paste layers caused by extensive crushing of paste surface particles during compaction.

The adhesion, or bond formation, between the paste and prebaked carbon materials during baking is also an aspect that may have to be considered. This can only be achieved if the paste contains, or liberates, enough binder during the carbonization process for binder coke bridges to form between the prebaked carbon surface and the paste. The mechanical strength of this bond will generally be considerably lower than in the surrounding materials. Potylitsyn *et al.* [5] found that the highest bond strength between the prebaked block and baked paste was obtained when the green paste was well compacted and baked to about 900°C. A good "weld" between the paste and the block after baking ensures a better seal and reduces the probability of liquid penetration, but is, according to Franke *et al.* [6], not absolutely required.

PASTE SHRINKAGE DURING BAKING

All cathode construction materials will undergo dimensional changes, expansion or contraction, when subjected to temperature variations. Generally this has to be taken into consideration when the cathode is constructed. The reversible linear coefficient of thermal expansion (CTE) is defined by:

$$CTE = d\ell/(\ell dT) \quad (1)$$

where ℓ is length and T is temperature. While most lining materials show reversible thermal expansion/contraction behaviour, the thermal dilation of ramming paste is only reversible in baked paste and only at temperatures below its maximum heat treatment temperature.

The liquid state of the binder extends up to nearly 500°C and its solidification is revealed by a more or less pronounced shrinkage at higher temperatures. Most shrinkage in the temperature range 500-1000°C is owing to the fact that the binder coke is denser than the liquid binder and that the binder coke yield is low, usually in the range of 30-60 %. The binder/binder coke bridges will

shrink during carbonization and thus the whole carbon body. A well formulated aggregate, choice of binder and binder content can reduce this shrinkage considerably.

Some general rules apply as to the thermal dilation of coke/coal-tar (pitch) pastes during baking. According to Sandberg *et al.* [7] there is a definite trend toward higher shrinkage with:

- increasing amount of aggregate fine (milled) fraction,
- decreasing ratio of coarse (> 2 mm) to medium fractions,
- decreasing maximum size of coarse particles.

Some reasons for these effects are that an increasing amount of dust/fines in the aggregate will, due to its high surface area, necessitate an increased binder content and hence increased binder coke shrinkage during baking. On the other hand, an increased amount of coarse particles will require fewer binder bridges per unit volume and thus reduce this effect. The coarse aggregate will therefore act as a reinforcement of the baked paste, counteracting the shrinkage of the binder coke. This counteracting effect becomes greater the higher the content of coarse particles in the paste is and the closer the dry aggregate particles can be packed.

There are, of course, limits to what extent the paste formulation can be varied while still maintaining sufficient ramming properties and mechanical strength and integrity during and after baking. Low shrinkage may be found in some pastes where extensive particle crushing is experienced during ramming. This type of aggregate crushing need not be the type caused by some particularly mechanically weak particles in the aggregate (see previous discussion), but rather due to formulation deficiencies such as lack of binder matrix (binder + fines) or lack of an intermediate fraction that may better distribute the interparticle stress development and soften the impact of the ramming tools. Ramming pastes that behave like this can, however, easily be spotted in certain paste quality tests [2].

Experimental. The dilation experiments were carried out in vertical push-rod quartz dilatometers, shown schematically in Figure 6. The dilatometers were flushed with inert gas during the experiments in order to avoid oxidation of the specimens and interference between condensing binder vapours and the push-rod assembly. The gas entered the bell-shaped sample chamber through holes drilled in the quartz tube and exited through the eccentric tube where tar and pyrolysis products were deposited. The push-rod was a small diameter thin-walled quartz glass tube that minimized the external load on the samples. The relative dilation between the bell-shaped tube and the push-rod was picked up by a transducer and fed into a computer for data acquisition and handling. The temperature was increased from ambient to 950°C at a rate of 3°C/min, followed by 7 hours soaking time at the maximum temperature. The dilation during cooling to ambient temperature (3°C/min) of the baked samples was also recorded, but only a minor part of the cooling curve is indicated in some of the examples shown later.

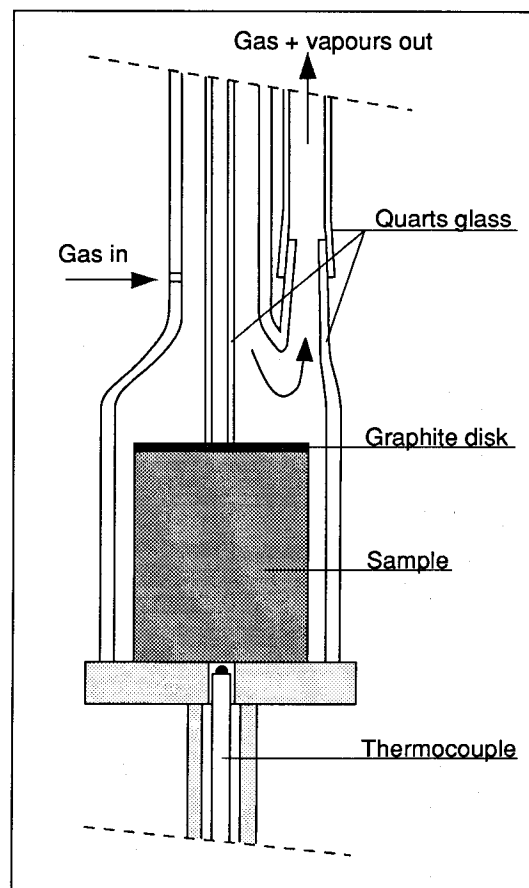


Figure 6. Schematics of the sample compartment of the quartz glass dilatometer.

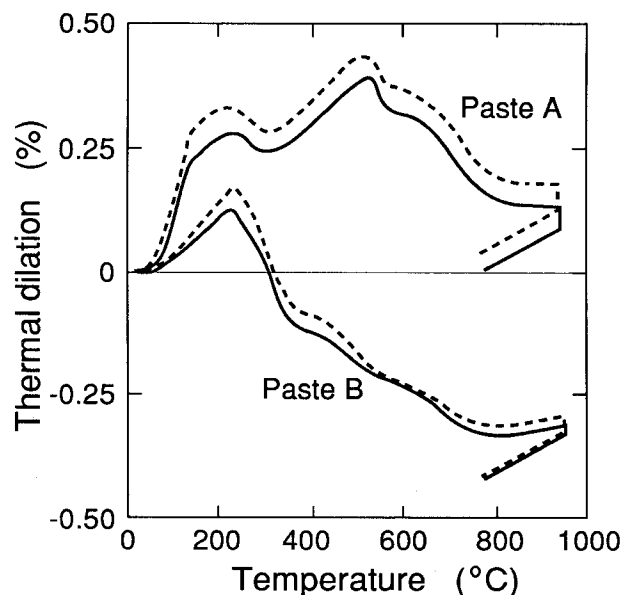


Figure 7. Typical reproducibility of the thermal dilation test. Free-standing samples rammed to green density 1500 kg/m³.

The pastes used in these experiments were commercially available cold type ramming pastes intended for use in the joints between the bottom blocks and in the peripheral seam. They were either compacted to the form of free-standing cylinders (40 mm diameter x ~50 mm height) or rammed into graphite crucibles (same paste density and dimensions). All pastes had anthracite based aggregates.

Laboratory experiments. During baking to the operating temperature, ramming pastes based on coal tar (pitch) binders will retain some plasticity up to about 500°C. Below this "solidification" temperature a certain degree of excess expansion or "swelling" or "slumping" is usually experienced.

The swelling behaviour is caused by pressure build-up in gases, binder vapours and pyrolysis products trapped within the paste. Fitzer *et al.* [8] found a correlation between increased bulk dimensions of green carbon bodies and increasing dimensional changes caused by swelling during heating. Some slumping upon heating may take place in free-standing paste samples but is not likely to be experienced in a packed joint or seam.

The reproducibility of paste dilation experiments on free-standing samples is satisfactory at temperatures above ~500°C, *i.e.* after "solidification" of the binder. This is illustrated in Figure 7 with the dilation curves of three similar samples of the same ramming paste. The reproducibility of the swelling and/or slumping behaviour in the plastic temperature range below ~500°C is usually less good. The latter is, however, not unexpected as these are very inhomogenous materials. It is also of minor importance in regard to paste failure in the cathode, it is the shrinkage behavior at temperatures above ~500°C that matters.

Baking of paste constrained by crucible walls may imitate paste dilation in the narrow joints between the bottom blocks during cell preheating, but can severely underestimate the shrinkage that takes place in the often much broader peripheral seam. Wall friction and sticking at temperatures above 500°C gives the appearance of lower

shrinkage during baking than free-standing ramming paste samples (Figure 8). It is interesting to note that Paste B (crucible) shows real shrinkage starting at temperatures close to 200°C.

The magnitude of swelling and shrinkage in pastes during baking is unpredictable and has to be tested for each type or brand. Experience has further shown that the thermal dilation of ramming pastes may suddenly change due to changes in the producers process variables or raw materials. This is often not relayed to the user, making it necessary to monitor the thermal shrinkage of the ramming paste that is used at certain intervals.

If thermal dilation is measured directly on green samples a certain degree of slumping (*i.e.* contraction in plastic paste) may be experienced in some pastes. The magnitude of slumping is caused mainly by gravity but pre-shrinkage of plastic paste due to binder volatilization may be responsible for part of it. This will, however, usually constitute an experimental nuisance encountered only in the laboratory and bear little relevance to the paste behaviour in the pot. The slumping can be reduced if some form of "conditioning" of the paste is performed prior to the dilation test. This is illustrated in Figure 9 which shows the dilation curves of two cold type ramming pastes compacted to similar densities and pre-conditioned at various temperatures. Pre-conditioning may, however, lead to an apparent reduced shrinkage in the paste measured from 500°C, with the possibility of underestimating paste shrinkage in the cathode.

Based on such experiments we consider the paste shrinkage most realistically evaluated from ~500°C and up to near cell operating temperatures by baking the compacted but non-conditioned sample continuously from room temperature at a rate approximating the temperature increase rate it is likely to experience during cell preheating. For practical reasons we use the heating rates described earlier and have chosen to define the shrinkage as the net linear contraction in the temperature range 500-950°C, including the isothermal contraction at the maximum temperature. These net linear shrinkage values

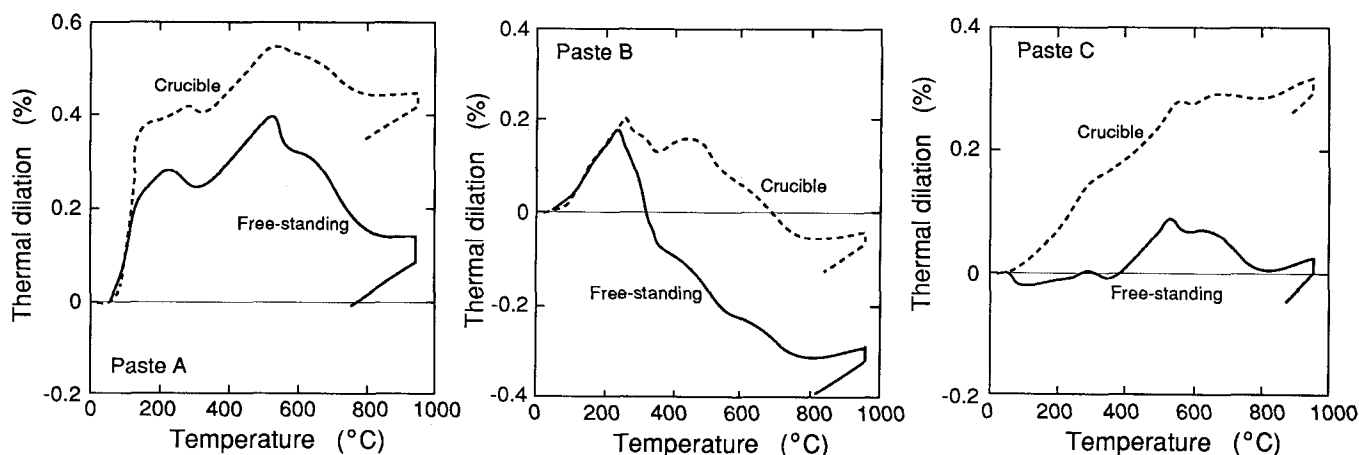


Figure 8. Thermal dilation of three cold type ramming pastes measured on constrained (crucible) and on free-standing samples heated in the temperature range 20-950°C. All samples were rammed to a green density of 1500 kg/m³.

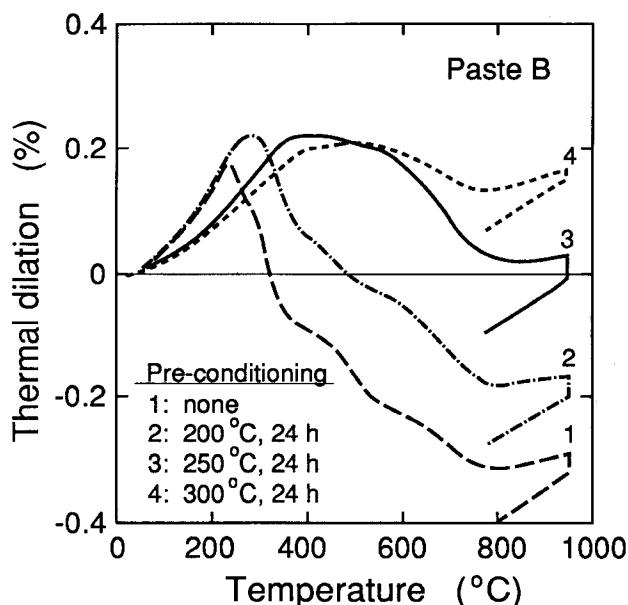


Figure 9. Swelling and shrinkage of a cold type ramming paste pre-conditioned at various temperatures (density 1500 kg/m³).

are shown in Table 1 for five ramming pastes that have been investigated. Even if the temperature that the paste will be baked to in the cell is below this maximum temperature, some additional and slow isothermal shrinkage will take place during operation. Only for very narrow seams or joints may the shrinkage be less because of wall friction.

Paste shrinkage in cathodes. The peripheral seam is vulnerable to the type of cracking shown in Figure 10. This crack pattern has repeatedly been observed in autopsied cathodes and also after preheating of cells, and is mainly caused by paste shrinkage during baking. The net thermal dilation of the carbon bottom pane (blocks + joints) can aggravate the cracking, but is not the major cause. If, for example, a paste with poor shrinkage characteristics has been used ($\Delta l \approx 0.4\%$), this kind of shrinkage could amount to as much as 40 mm total crack width *per* 10 m peripheral seam. The real total crack opening will normally be somewhat less than this calculated maximum due to other types of stress release mechanisms, but a paste with high shrinkage may result in enough crack formation, and early metal and bath penetration, to seriously decrease the pot life. An example of this kind of failure, taken from an autopsied cathode, is shown in Figure 11. The vertical crack surface through the peripheral seam is evident from its coating with aluminium carbide and bath components.

Table 1. Net linear shrinkage of room temperature ramming pastes from 500 to 950°C. Soaking time 7 hours at 950°C.

PASTE	A	B	C	D	E
SHRINKAGE	0.31	0.15 a)	0.09	0.14	0.41

a) Underestimated due to contraction in 'plastic' region

Differences in thermal dilation of the prebaked carbon bottom and the peripheral seam during preheating and early cell operation may lead to vertical crack formation in the paste parallel to the sides of the carbon pane, or as usually seen, gap openings at the vertical interface between the bottom block and the paste.

The combined action of block expansion and paste swelling in the temperature range below 500°C will slightly compact (or extrude) the paste in the seam. Any interfacial gap opening in this part of the lining is therefore likely to take place in the temperature range where the paste is subject to shrinkage. Furthermore, due to the high ratio of block length to paste width these interfacial shrinkage gaps can only be formed if the carbon bottom is heated unevenly, *i.e.* that the carbon bottom pane has undergone most of its thermal expansion when the paste starts to bake. This is usually the situation during preheating of cathodes, whether it is by gas-, coke resistor- or metal

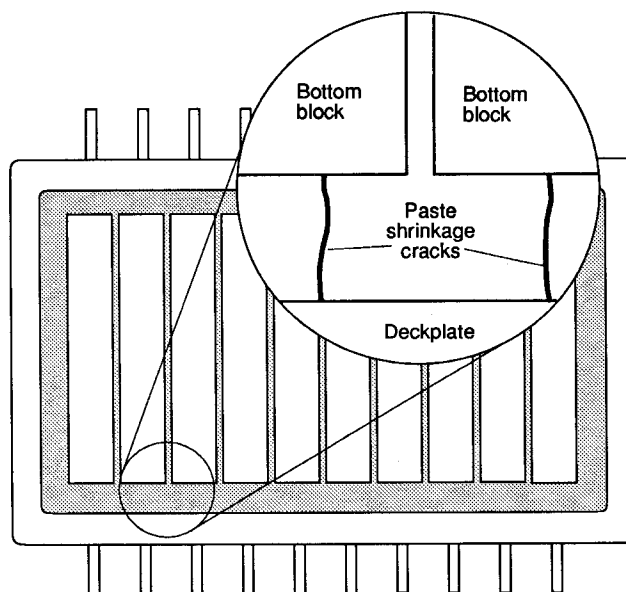


Figure 10. Typical pattern of shrinkage cracks found in the peripheral seam after excessive paste shrinkage.



Figure 11. Cathode failure caused by excessive shrinkage of ramming paste.

preheat. The peripheral seam is usually protected by some type of insulation or banked with cryolite or crushed bath during preheating and most of the heat is transferred to the paste indirectly through the vertical face of the bottom block.

Figure 12 shows the approximate temperature distribution in a cathode measured after a gas preheat. Four of the positions where the temperature was monitored are indicated (circles 1-4). The corresponding temperature *versus* time curves are shown in Figure 13. It is seen that it takes about 12 hours from the cell is started until all the paste in the peripheral seam is "solidified", *i.e.* the temperature has reached at least 500°C. Preheating temperatures and -temperature distribution in cathodes prior to start-up may, however, vary considerably from

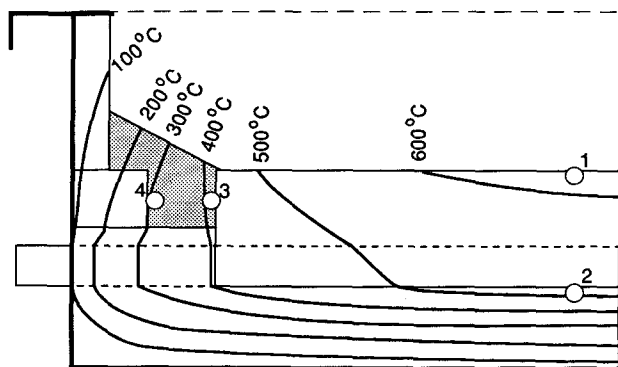


Figure 12. Isotherms measured in a cathode after gas preheat. Shaded area is peripheral ramming paste seam. Some positions for temperature measurements (1-4) are indicated.

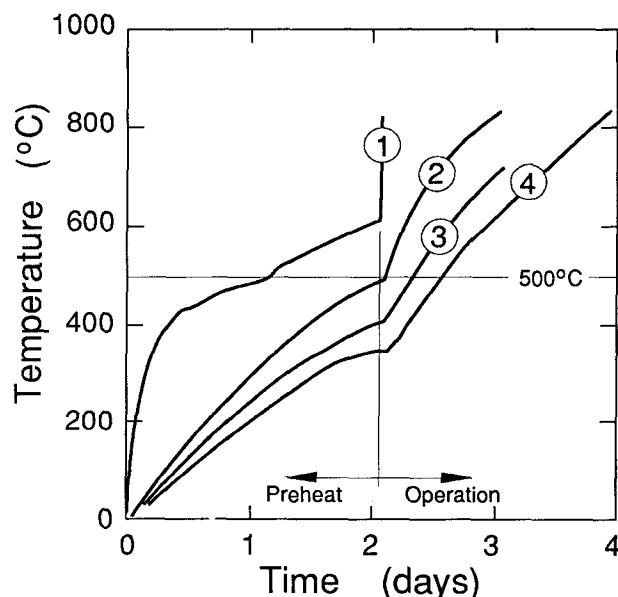


Figure 13. Some temperatures measured in the cathode during preheating and early cell operation. Numbers 1-4 correspond to positions indicated in Figure 12.

plant to plant depending on equipment, method, experience and philosophy.

In order to be on the safe side the peripheral seam should be made as narrow as possible while still being able to absorb most of the thermal expansion of the bottom blocks by plastic deformation. The maximum safe width can be calculated from thermal expansion and shrinkage data for blocks and paste and by knowing the temperature distribution and rate of temperature increase in the lining during preheating and early operation. A good approximation can be obtained fairly simple by using average temperatures in block and seam while a more accurate calculation can be performed using finite element methods.

CONCLUSIONS

- Over-compaction of ramming paste may give extensive crushing of aggregate particles.
- Crushing of aggregate particles during compaction will result in poor mechanical properties and stratification of rammed parts after baking .
- Some ramming paste aggregates consist of considerable amounts of very weak coarse particles. Such pastes should be avoided or installed with care.
- Measurements of electrical resistivity and/or mechanical strength of baked paste specimens as a function of green density will indicate safe compaction (green density) range.
- Shrinkage during baking should be measured regularly on ramming pastes prior to installation in cathodes.
- The peripheral paste seam should be made narrow in order to minimise failures caused by paste shrinkage during baking.

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