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Prebaked Anodes Cracking at Forming - Reasons and Solutions

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Abstract

Avoiding prebaked anodes cracking during forming depends on two principles: avoid trapping pressurized air in anodes during forming and adjusting anode cohesion forces to retain anode internal stresses. Consequences of misinterpretation of these two principles explain most cracking problems related to forming of prebaked anodes. A good understanding of these two principles facilitates the diagnostics of anode cracking problems and finding ways to improve anode properties by adjusting parameters of processes before forming and those of forming process itself.

Keywords: Prebaked anode cracking, optimal binder, capillary bridge, binder viscosity.

1. Introduction

Prebaked anode forming is an important step in obtaining a good baked anode quality for use in electrolysis pots. Part of this step looks like black magic, because it is often difficult to find explanations to observed behaviours like appearance of cracks. It is common to stay in comfort zones, far from limits where unexplainable behaviours happen.

Prebaked anode quality improvement imperatives, tied to potline current increase or tied to raw material quality degradation, sometimes oblige one to navigate in areas where quality problems start afflicting anodes. A better understanding of physical changes that happens during anode compaction is then required to modify forming process parameters themselves or to modify previous processes parameters to correct cracking problems as they appear.

2. Cracks Formation Principles

Understanding two principles is needed to understand crack formation mechanisms during anode forming:

- Avoid trapping pressurized air in anode during forming;
- Adjusting cohesion forces which hold the anode together to retain internal anode stresses.

2.1. Avoid Trapping Pressurized Air in Anode During Forming

Why is air trapped in the anode during forming? Air is trapped when open pores transit to closed pores.

Optimal binder level is binder level that saturates aggregate after unmolding from the vibrocompactor mould or press mould [1, 2] and it is usually the target to reach. This corresponds to maximum binder quantity the anode structure can retain. If anode is under saturated, it lacks binder and there are pockets of space filled with air instead of binder. This gives a baked anode density lower than the one obtained if the anode was saturated. If anode is oversaturated, this means that aggregates float in the binder and the excess binder will be exuded at baking when temperature will be high enough to make binder flow freely above 200 °C and before binding the cokefaction.

Binder, that anode structure cannot hold, will come out of the anode which leads to the packing coke sticking to the surface of baked anode. When the binder comes out, the volume formerly occupied by binder will be filled by air, reducing baked anode density below what would be achieved at anode binder saturation. (Figures 1 a, b and c, adapted from Reference [3].)

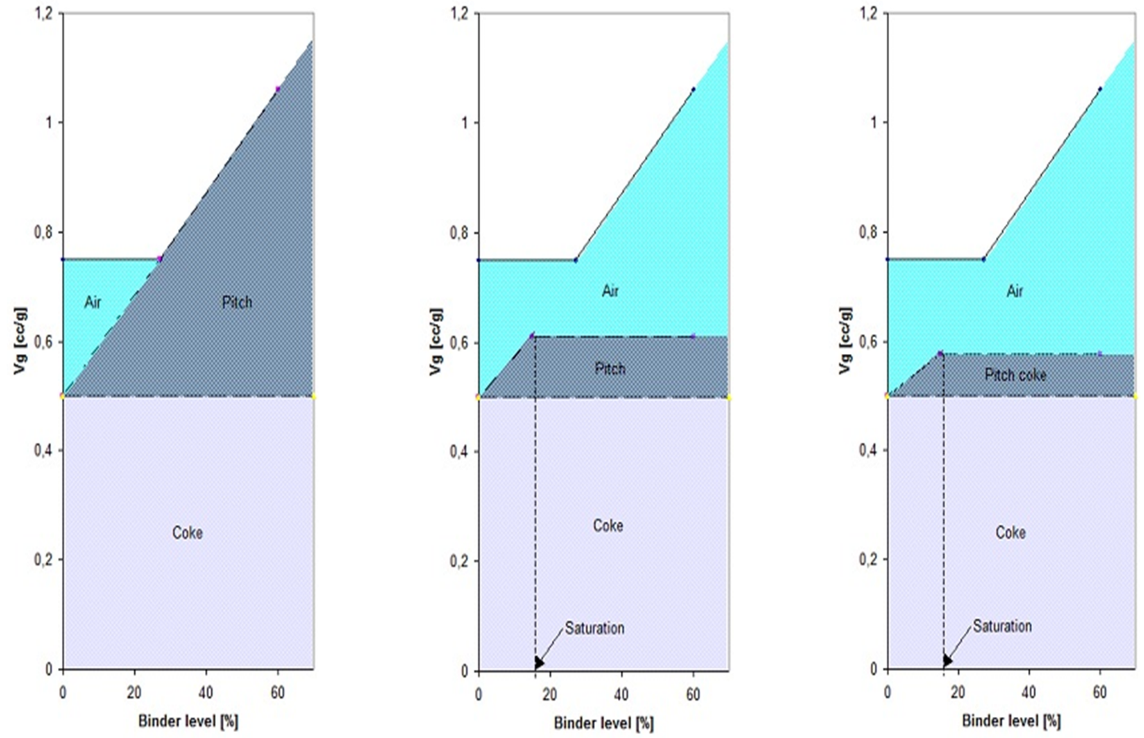

Figure 1a, Volume of green anode, simplified from figure 10b, Reference [3]

Figure 1b, Volume of green anode at 200 C in baking furnace

Figure 1c, Volume of baked anode, simplified from figure 13b, Reference [3]. Shrinkage neglected for clarity.

Figure 1. Creation of anode porosity and low anode density.

During forming stage, the paste goes from an undersaturated state to a saturated state, to end in an oversaturated state. To be saturated after unmolding, the paste has to be oversaturated in mould during forming. This has important implications.

While forming, when the paste starts in an undersaturated state, pores containing air giving low green anode density are open. This means that, during undersaturated stage, air has paths to come out of paste, permitting anode densification. When anode comes to an oversaturated state, this means aggregate floats in binder. This implies that pores containing air, transit from an open state to a close state and the air remains trapped in the pores. Green anode densification then results from compression of air contained in pores, an elastic reversible compression of aggregates themselves [1], which does not contribute to anode densification.

Compaction advances by paste plastic deformations. The aggregate becomes more compact by reduction of pores volume by increasing air pressure in closed pores (and reversible elastic deformation of aggregate matrix) when in oversaturation state. Each time forming pressure lowers, between press forming pressure, and between each vibrocompactor counterweight hit, pore pressure lowers, because pores regain their volume partly. If internal pressure of the pores generates stresses higher than anode cohesion forces, cohesion forces fail, causing microcracks.

If the number of microcracks becomes large enough, they gather into macroscopic size cracks, visible to the naked eye. Crack network may supply paths for air to escape from green anode, allowing a higher green and baked density, but this is detrimental for electrical conductivity of baked anodes. This may explain why anode electrical resistivity, which normally lowers when baked anode density rises, starts rising after a compaction threshold.

Cracking occurs in two steps. When relaxing compaction force, between press forming pressures or between vibrocompactor counterweight hits, green anode volume augments in mould allowing cracking of green anode. At unmolding, forces pushing against mould are relaxed and have to be retained by green anode. If supplementary stresses are bigger than anode cohesion forces, cracks will appear, or more cracks will appear, if cracks are already present.

However, green anode oversaturation does not happen all over the anode in one shot since the oversaturation progresses from zones already oversaturated to saturated zones, then to undersaturated zones. If undersaturated zones end up surrounded by oversaturated zones, air from undersaturated zones will not be able to escape, retarding or stopping anode densification.

2.2. Adjusting Cohesion Forces to Retain Internal Anode Stress

What holds an anode together? Capillarity; capillary forces implicated in anode cohesion are the same as the ones that hold sand castle together. Capillary forces come from capillary bridges between particles. Meniscus of liquid forms between particles wetted by this liquid. Force of capillary bridges depends on liquid viscosity. With water, viscosity does not vary much between freezing and boiling. Molasses are used as binder in making of foundry sand moulds, because the viscosity of molasses is higher than water viscosity, resulting in a “sand castle”, a mould, more coherent, less fragile.

In the anode case, pitch is a vitreous liquid and the viscosity changes by a factor of two with each 10 °C change (Figure 2). Pitch with 110 °C softening point is essentially solid at temperature below 100 °C. It is barely pumpable with a gear pump at 160 °C. It is easily pumpable at 180 °C. It is difficult to pump over 220 – 250 °C, because its viscosity is very low. Pitch with 80 °C softening point flows at room temperature, but VERY slowly, as seen in pitch drop experiment, the longest scientific experiment still running (9 drops fell in 85 years, see https://en.wikipedia.org/ wiki/Pitch_drop_experiment).

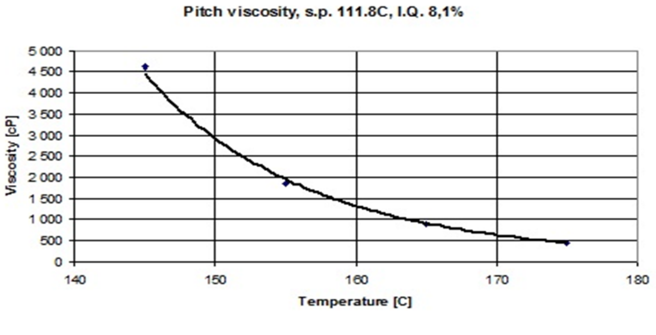

Figure 2. Pitch viscosity vs temperature graph, data taken from Reference [4].

It is possible to raise or to lower capillary cohesion force, which holds green anode together, by changing pitch temperature, which, in turn, affects the rigidity of capillarity bridges by modifying liquid viscosity.

2.3. Explanation of Common Causes of Cracking

Knowing these two principles, the pieces of the puzzle come in place.

Let us assume an unevenly filled anode forming mould. There is a paste hump at one end of the mould and forming starts. What happens? As the press rams or vibrocompactor counterweight is lowered, keeping it levelled, paste hump undergoes a larger compaction force than the paste at the mould end where there is less paste. The end with paste hump will become oversaturated before the other end, leading it to cracks, when pressure is released during forming and at unmolding. This is why a levelled paste in mould is preferable.

Let us now suppose that the paste in the mould is levelled, but the paste at one end of the mould is hotter than the paste at the other end of the mould. What will happen? As stresses undergone by paste during forming, at both ends of the mould are equal, the spring back will be equal. As anode cohesion forces depend on pitch temperature, the hot end of the block will be weaker than the cold end, resulting in cracks at the hot end. This is why paste temperature should be uniform.

The bottom of stub holes represents a special case. If the paste is levelled in the mould, localized pressure under the stub-hole formers may lead to the appearance of localized oversaturated zone under stub-hole formers, long before it appears in other parts of the block. This may result in laminated, flaky, bottom of stub holes because of cracks resulting from early oversaturation.

3. How to Avoid Cracking

There are two families of ways to reduce cracking caused by “excessive” oversaturation:

- Retain stresses caused by “excessive” oversaturation;
- Reduce stresses to be retained; this family can be subdivided into two subfamilies:
    - Ways that reduce green anode density;
    - Ways that increase green anode density.

3.1. Retaining Stresses Caused by “Excessive” Oversaturation

This family of ways works on the binder of the anode, the pitch. Maximization of number of capillary bridges is a first way to increase block capacity to retain stresses. As mentioned earlier, capillary bridges form between particles wetted by liquid. This implies that maximum surface area of coke particles must be wetted by pitch. This has already been known for a long time. Wetting is maximized by preheating the aggregate and the pitch at similar temperatures before mixing, raising mixing temperature, increasing mixing time and increasing shearing between particles in mixer sometimes referred as increasing mixing energy.

If increased mixing energy fractures aggregate during mixing, it may be possible that free available binder, at mixing stage where fracture occurred, is insufficient to wet new surface area created. This may result in decreasing of block ability to retain stresses, which may cause anode cracking. As incoming coke is most of time a mix of coke sources, which can lead to problems. Some coke sources may be more fragile than others and using the same mixing energy will fracture them although particles of other coke sources may stay intact. This may cause intermittent cracking crisis whose cause may be difficult to find. Lowering mixing energy may be a short-term solution to be tried for this problem.

It is also possible to increase binder viscosity by loading it with very fine coke (minus 30 µm), called "filler" in Reference [1]. An optimal "filler" level, by increasing "filler-pitch" mix viscosity, at mixing temperature, will result in an increase of paste viscosity at forming temperature. But this may be a double-edged sword. By increasing "filler-binder" mix viscosity, it usually results in a more difficult densification.

Reduction of forming temperature increases viscosity of the liquid forming capillary bridges. This way of doing, as the preceding one, also increases the difficulty to densify the paste, because the paste viscosity increases.

Using the same logic, i.e., using a higher softening point pitch and forming at the same, or slightly higher forming temperature than lower softening point pitch, also gives stronger capillary bridges. A point to remember is that the mixing temperature has to be raised, because a higher softening point pitch requires a higher mixing temperature to wet aggregate.

3.2. Reducing Forming Stresses

3.2.1. With Density Reduction

This family of means is usually used as last resort when it is required to rapidly stop cracking. It includes means of reducing the forming energy directly.

- In a press by:
    - Reducing forming pressure, or
    - Reducing the number of forming strokes in case of forming with multiple strokes;
- and vibrocompactor stresses by:
    - Reducing vibration time,
    - Reducing vibration speed,
    - Reducing counterweight pneumatic pressure or by removing it completely if pneumatic counterweight pressure is present, or
    - Reducing unbalance of ex-centric weights of vibrocompactor.

However, these solutions are not very popular and should be used only in case of major cracking crisis, to survive until a solution to come back to normality is found.

3.2.2. With Density Increase

To reduce stresses while increasing densification, the usual method is to reduce the amount of air in the paste. This can be performed at many paste manufacturing stages.

The first and very evident way to lower air content in the paste is to start with already dense aggregate, either by choosing a dense coke source or by separating dense coke from porous coke in aggregate [5]. In this case, the dense coke is used as aggregate, the porous coke is crushed using ball mills to constitute fine fraction, removing problematic porosity by crushing.

Intensive primary mixing allows penetration of pitch and fine coke ("filler") mix in grain open pores, removing air from the pores.

Secondary mixing at lower temperature allows paste pre-densification [6] by agglomerating pitch-coated grains in paste lumps, containing little air.

Reaching anode saturation during forming may be delayed by reducing binder level. Indeed, when forming compaction forces increase, optimal binder level lowers [1]. By delaying of the onset of anode saturation, the undersaturated period during forming is lengthened, allowing more air to escape. This mean is not easy to apply, because optimal binder level changes with raw material properties, wetting level obtained during primary mixing, pre-compaction level obtained during primary and secondary mixing, forming temperature and compaction energy supplied during forming, which can change depending on equipment behaviour. A method to stay at optimal binder level is to hunt it in real time, to take into account all these variations [7]. Such an algorithm allows compensation of lots of variation causes, on which it is difficult to have total control.

The last way to reduce air quantity in the paste is to remove it at forming time by using vacuum. This vacuum is performed before forming, before the press ram reaches the paste. Vacuum is maintained during all forming time with vibrocompactors.

By reducing air quantity in the paste during forming, forming stresses are reduced and, as a consequence, forming temperature may be higher, which explains the temperature range in Table 1. Atmospheric press generates biggest stresses in anodes, from which very low forming temperature, 105 °C to 115 °C. A vacuum high energy vibrocompactor may work at primary mixing temperature, 170 °C to 180 °C, because internal stresses in the anode are very low.

Table 1. Forming temperature ranges in relation with forming technology (pitch softening point is 110 °C).

Forming technology	**Forming temperature ranges [°C]**
Atmospheric press	105 - 115
Vacuum press	120 - 130
Atmospheric vibrocompactor	140 - 150
Vacuum vibrocompactor	160 - 170
Vacuum vibrocompactor with counterweight pressure	170 - 180

3.3. Other Sources of Cracking

Even when all possible precautions are taken, during paste manufacturing or green anode forming, it is not always possible for anode blocks to reach baking intact. Other sources of stresses may crack anodes. Among usual suspects, cracking may be caused:

For a press:

- By wear of mould wear liners, by cracking of mould wear liners or by missing part of wear liners;
- Asymmetric unmolding, mould lowers one side before the other, or ejector is not level and pushes asymmetrically when unmolding;
- Too a fast ram rising, at unmolding, that acts as a syringe ram, pulling anode top upward; or
- Paste sticking to bonnet former profile or to stud hole formers.

For a vibrocompactor:

- By mould wear, as for press, or mould welds cracking, this gives it undesired flexibility;
- Asymmetric unmolding, mould raises one side before the other at unmolding;
- Paste sticking to bonnet former profile or to stud hole formers;

- Deformation caused by level differences during anode transfers between equipment to cooling trays;
- Squeezing anode between anode pusher and an obstacle when ejecting anode from vibrocompactor table or transferring anode using pneumatic or hydraulic cylinders, with either ejector cylinder lengthens too much or an obstacle usually not there appears; or
- Deformation of the anode caused by deformed cooling trays. They are cambered or warped, a problem caused by repetitive thermal stresses.

4. Conclusion

Manufacturing a dense and crack free anode is not easy. The number of variables that can affect anode cohesion at forming is important and mastering them all requires a good understanding of principles used during anode paste and blocks manufacturing. Even with rigorous control, it is still possible that a variable escapes operation or process personnel attention.

Need for dimensions or property changes of anodes supplied to electrolysis, or important changes in anode raw materials, may also deviate from usual process parameters, obliging to venture outside comfort zones where behaviour of paste, equipment or green anodes is known.

Among ways to avoid or to solve these problematic situations, there are several options:

- Formal technical training,
- Technical self-training, through reading technical articles in anode manufacturing,
- Through plant structured testing, to test process limits, when possible,
- Peer meetings, through other plant visits, inside or outside the company, or during conferences,
- Attendance to technical conferences, and
- Call to people who already encountered problems happening in your plant.

Problem solving use may sometimes be pertinent, but without adequate knowledge among team members of principles driving the processes, problem solving may be of little use. As Louis Pasteur said:

“*Dans les champs de l'observation, le hasard ne favorise que les esprits préparés.”*

“In the fields of observation, chance favours only the prepared mind”.

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