

COOLING OF GREEN ANODES AFTER FORMING

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ABSTRACT

When green anodes are formed at high temperatures, they exhibit a low mechanical stability. For this reason they need to be cooled. When the anodes are cooled too intensely, surface fissures are generated due the shrinkage of the crust. However, insufficient cooling may cause the anode to be damaged during subsequent handling, storage and processing.

Three cooling methods exist in practice: water spray, water bath and air. Anodes vibrated at temperatures well above the pitch softening point need to be cooled in a water bath whereas pressed anodes can be cooled by the ambient air. In this study, the optimum cooling conditions are defined using a mathematical model. Practical guidelines are given to optimize the logistics of anode handling, storage and further processing.

INTRODUCTION

Green anodes are formed either by a press or a vibrocompactor [1]. Due to the softness of the binder pitch, green anodes exhibit a low

mechanical stability after forming and therefore need to be cooled. This is usually done in two stages.

In a first stage, hereafter referred to as the main cooling process, the anode is commonly cooled by water spray or immersion in a water bath. Thereby only a small outer crust is cooled down due to the low temperature conductivity of the material (approximately $1.2 \cdot 10^{-6} \text{ m}^2/\text{s}$). Depending on the anode size, it takes an hour or more before the heat starts to flow from the center towards the surfaces. The cooling process is thus limited by the temperature conductivity of the material and cannot be accelerated.

In the second stage the anode is usually cooled in the ambient by free air convection. In contrast to the main cooling process the limiting factor is the heat transfer from the surfaces to the ambient.

In practice the following problems can occur after forming [2]:

- Formation of convex anode surfaces directly after forming (referred to as slumping) before cooling due to inappropriate recipe parameters (e.g. pitch content, dust content and fineness) and forming temperature [3]. This is independent of the cooling process and will therefore not be treated in this study.

- Formation of hairline cracks due to shock cooling resulting in excessive shrinkage at the surface while the center remains hot; these cracks are closed during subsequent cooling (and thus shrinkage) of the anode center, but remain as surface flaws.
- Reheating of the anode surfaces due to the stored heat in the center of the anode and subsequent slumping during the transport to the anode storage or bake furnace
- Formation of vertical cracks originating at the surface due to tensional stresses caused from applying a bending moment by uneven roller conveyors or transfer equipment
- Damage of the anode surface by the clamping device during anode handling
- Deformation of the surfaces of the bottom anodes, when they are stacked for storage
- Release of frozen stresses induced by the forming and cooling process and formation of vertical cracks in the critical phase of pitch devolatilization during baking

The anode forming temperature is the key parameter of the cooling process and depends on the forming method [4]. For pressed anodes this temperature corresponds to the (Mettler) softening point of pitch, i.e. 100 to 120°C. For vibrated anodes the forming temperature is about 40°C higher than the softening point, with the highest temperatures being above 170°C. When the anodes are formed under vacuum, the temperature can be raised by 10 to 30°C.

When the temperature of the green anode is close to or above the pitch softening point, the mechanical stability is very low. The compressive strength gives a good indication about the susceptibility of the anode structure. Figure 1 illustrates that the compressive strength of the green anode is stable up to about 50°C and decreases dramatically, when the material starts to exhibit pronounced elasticoviscous behaviour [4]. The critical temperature can vary depending on the pitch softening point.

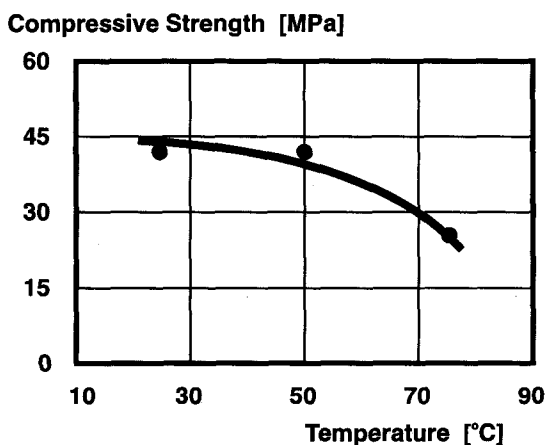


Figure 1: Compressive strength of a green production anode as a function of its temperature, pitch softening point 107°C

The material behaviour of the green anodes strongly depends on the temperature level, which dictates the boundary conditions of the cooling process. The goal of this paper is to define the required boundary conditions in order to realize optimum cooling without causing any of the above mentioned problems.

EXPERIMENTAL

Table I shows a selection of physical properties measured on green anodes at room temperature. The tests have been performed using the standard testing equipment for baked anodes, as described in [5]. These test methods are designed for baked anodes assuming linear elastic material behaviour. However, green anodes exhibit a nonlinear, elasticoviscous behaviour with partially irreversible plastic deformation before fracture occurs [4]. Therefore the mechanical properties listed below are approximations.

Table I: Physical Properties of Green Anodes at Room Temperature

Properties	Unit	Typical Range
Apparent Density	kg/dm ³	1.60 - 1.70
Flexural Strength	MPa	5.5 - 8.0
Compressive Strength	MPa	30 - 50
Elasticity Modulus	Static GPa	4.5 - 8.0
	Dynamic GPa	9.5 - 12.0
Coeff. Thermal Expansion	20-100°C 10 ⁻⁶ /K	20 - 60
Fracture Energy	J/m ²	70 - 120
Thermal Conductivity	W/mK	1.6 - 2.1

The CTE of the green anode is almost one order of magnitude higher than for the baked anode [6]. Assuming linear elastic behaviour, such a high CTE would soon create stresses well above the critical strength when the temperature is varied. As in practice the material withstands these stresses, this is also an indication that for temperatures above 50°C the material exhibits elasticoviscous behaviour which releases the stresses.

Temperature measurements have been performed on green fullsize production anodes (LxWxH: 1650x720x600 mm) directly after forming to study the efficiency of different cooling processes. All anodes were vibrated at a temperature of 155 ± 5°C. The boundary conditions of the tests were as follows:

- Forced air convection: Ambient temperature 8°C, wind 2 m/s
- Water: Water temperature 10°C, free convection, 16 hours
- Water spray for 20 minutes and subsequent forced air convection: Temperature of water spray 23°C, ambient temperature 8°C, wind 2 m/s

The small breeze in the hall turned the free air convection into a mixed forced convection which increases the heat transfer considerably. Regarding the water bath, the anodes are normally moved which also increases the heat transfer. In the test the anode was stationary, therefore free convection applies. Figure 2 shows the results obtained from the temperature measurements taken in the center axis of the green anode, 145 mm below the top surface. Taking into account the particular test conditions, the performance of the different cooling methods can be ranked as follows: Realistic water bath > water spray = forced air convection (high velocity) >> free air convection.

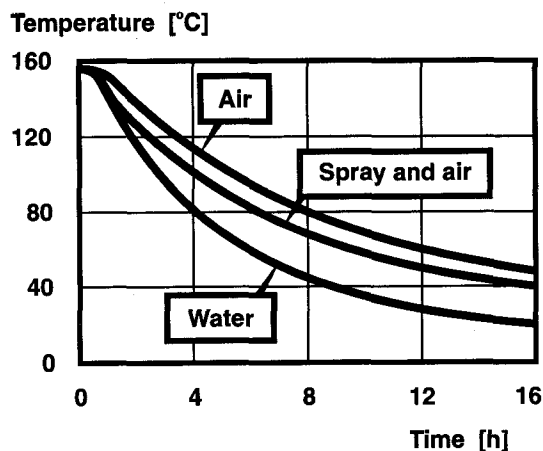


Figure 2: Comparison of different cooling methods

Figure 3 shows the temperature evolution of a green anode cooled in a water bath. The temperature was measured in the center of the anode and 145 mm below the top surface with similar boundary conditions as described above. After the first hour of cooling the center of the anode still exhibits the forming temperature of 155°C and also the layer 145 mm below the top surface remains very hot with 140°C. After 16 hours a quasi-uniform temperature is reached.

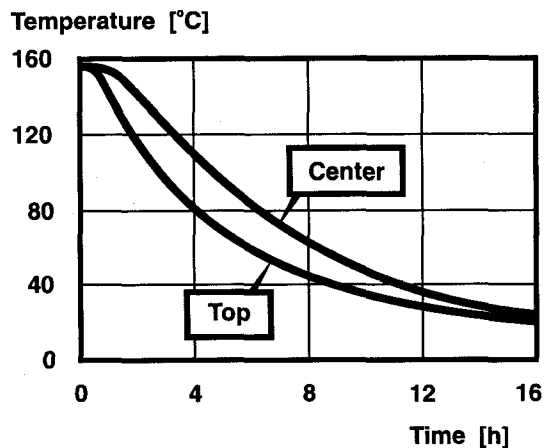


Figure 3: Temperature evolution of a vibrated anode cooled in a water bath (free convection)

THEORY AND MODEL

Temperature Distribution

A simulation program has been developed to predict the anode temperature during cooling. The theory can be summarized as follows.

The cooling of solid bodies is a heat diffusion process. For isotropic solids with constant material properties this process can be described by the well known Fourier Equation [7]:

$$\frac{dT}{dt} = \alpha \cdot \Delta T \tag{1}$$

where:

T	[K]	Temperature
t	[s]	Time
α	[m ² /s]	Temperature conductivity
Δ		Laplace operator

The diffusion coefficient α is commonly referred to as the temperature conductivity, which is proportional to the thermal conductivity and inversely proportional to the apparent density and the specific heat capacity [7].

$$\alpha = \frac{\lambda}{\rho_{app} \cdot c_p} \tag{2}$$

where:

λ	[W/mK]	Thermal conductivity
ρ_{app}	[kg/m ³]	Apparent density
c_p	[J/kgK]	Specific heat capacity

The boundary conditions for each of the surfaces can be developed with the energy balance of the heat flow from the center to the surfaces and from the surfaces to the ambient. The heat transfer coefficients are calculated with correlations found in [7] and [8].

A maximal heat transfer coefficient of up to 1000 W/m²K can be expected by immersion in a water bath. For cooling by free air convection the maximal heat transfer coefficient is significantly lower and ranges between 1.5 and 5 W/m²K, depending on the surface orientation. Air cooling gets more efficient with forced convection with coefficients of up to 100 W/m²K at a (theoretical) air velocity of 30 m/s. This corresponds to the level that can be expected for spray cooling.

The cooling process is limited by the temperature conductivity of the green material. Therefore an increase in the heat transfer

coefficient does not automatically increase the cooling efficiency. The analysis of the heat flux density at the surfaces shows that cooling by immersion in a water bath, spray cooling and forced convection air cooling have a common asymptote, which is reached after 20 to 30 minutes cooling [4].

The parabolic partial differential equations used for the model have been discretized in time applying a three dimensional grid to the anode with constant mesh size in each direction [9]. All diagrams presented hereafter were calculated with a 2 cm mesh size and with a time step of 2 s.

Integral Temperature

Based on the temperature distribution of the anode, the **integral temperature** T_I can be calculated for any point of time. This integral temperature can be regarded as the mean temperature of the anode. The practical relevance of the integral temperature is the following: When the cooling process of the anode is interrupted at a given point of time and the anode is completely insulated (which represents the worst case for anode storage), the anode will eventually reach the integral temperature at any point.

The maximum allowed temperature that shall be reached during reheating is defined as the **maximum integral temperature** $T_{I_{max}}$. The elasticoviscous material behaviour of the green anode at elevated temperatures implies to include the Mettler pitch softening point in the definition of $T_{I_{max}}$:

$$T_{I_{max}} = \text{PSP} - 10^\circ\text{C} \quad (3)$$

where:

$T_{I_{max}}$	[°C]	Maximum integral temperature
PSP	[°C]	Mettler pitch softening point

To avoid the problems mentioned in the introduction, the cooling time needs to be adjusted in such a way that $T_{I_{max}}$ is reached before the anodes are piled for storage. The required cooling time is a function of the forming temperature, the anode size and weight and the type of cooling.

In the following different configurations of anode cooling are compared with each other and checked for the suitability.

VERIFICATION OF THE MODEL

Tests in two anode plants have been performed to verify the model and simulation program. Anodes with a weight of 500 kg and 1'000 kg have been cooled by free and mixed forced air convection, by

spray and by immersion in a water bath. The measurements agree well with the simulations (see figure 4). The diagram shows the temperature evolution of a 1'000 kg anode cooled by forced air convection with similar boundary conditions as mentioned above. Other tests carried out with water bath and spray showed results being in similar good agreement with the model as for air cooling.

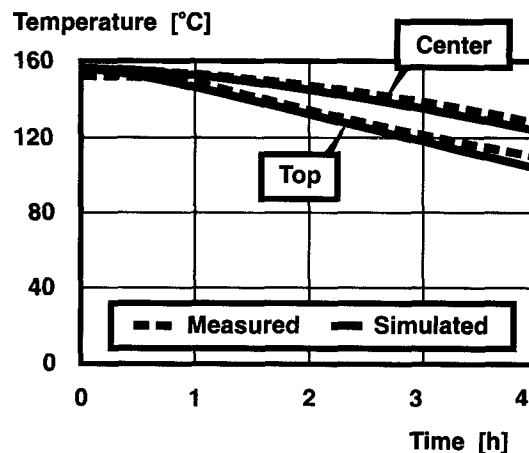


Figure 4: Comparison of the simulation program with the temperature measurement of an air cooled anode

RESULTS

Comparison of Water Bath and Water Spray

Figure 2 shows that the water spray and water bath exhibit similar cooling performances in a first phase. This may astonish because due to the vapourization of the water film an additional amount of heat is removed from the anode surface. In fact the vapourization decreases the surface temperature very quickly below 100°C which instantly stops this mechanism. Then the heat transfer coefficient for spray cooling drops even below the level for the water bath.

The equipment for water spray cooling (including cooling tunnel and water treatment system) requires an investment of US\$ 2 to 3 Mio. The maintenance cost is fairly high due to the corrosive attack of flux impurities (salts) from the butts in the water to the nozzles and other metal constructions. Maintenance work in the cooling tunnel is difficult because of the limited accessibility.

In a water bath, efficient and well controlled anode cooling can be obtained with counter current flow and a heat exchanger which requires a relatively small amount of water. The investment cost is 3 to 5 times lower (approx. US\$ 0.5 Mio.) and the maintenance is practically negligible. Considering the characteristics of water spray cooling and the related cost for investment and maintenance, water bath cooling has thus some distinct advantages.

Shock Cooling (Quenching)

The comparatively high CTE of green anodes makes them sensitive to thermal shock at low temperatures where the hard pitches are brittle [9]. Rapid cooling can cause shrinkage cracks at the surface due to tensile stresses. The fissures are mostly invisible after the block reaches a uniform temperature, but may show up again after baking. Excessive cooling can be achieved when a hot green anode is surrounded by a cold, turbulent water layer (as it can happen in the winter time with a strong water spray or a turbulent water bath). With subcooled boiling a heat transfer of 10'000 W/m²K and higher can result at the beginning of cooling [4]. Figure 5 shows a water bath configuration that allows efficient cooling without risking thermal shock problems.

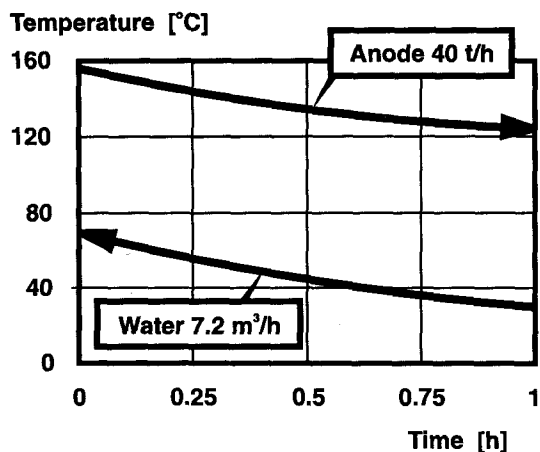


Figure 5: Energy balance of water bath

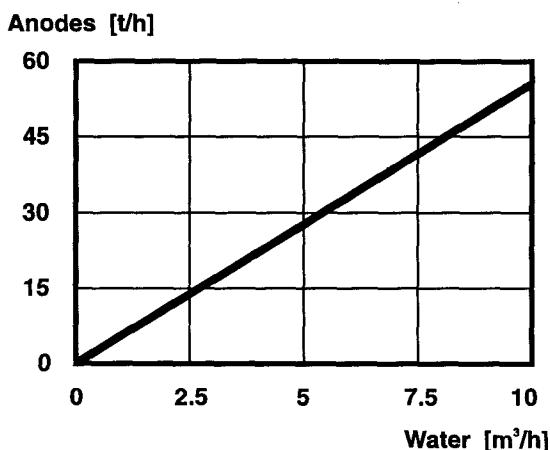


Figure 6: Cooling water requirement based on anode production rate; expected cooling time 1 h

To avoid shrinkage problems, the anodes should be cooled with warm water at their entrance to the bath. Based on the mechanical behaviour of the green anodes a water temperature of 70°C is ideal. Simulations have shown that no significant loss of cooling

performance occurs [4] for this rather elevated temperature of the cooling medium. Figure 6 illustrates that a relatively small amount of water is required to cool green anodes with the following boundary conditions:

- Anode integral temperature: In: 155°C Out: 125°C
- Water temperature: In: 30°C Out: 70°C
- Anode size: 1.6 x 0.7 x 0.6 m
- Anode weight: 1'000 kg
- Specific heat capacity of green anode: 1'000 J/kgK
- Specific heat capacity of water: 4'183 J/kgK

Reheating of the Surfaces

After the main cooling process the anodes are commonly further cooled down by free air convection. The limiting factor then changes from the heat transport in the anode body to the heat transport from the surfaces to the ambient. Then the surfaces may reheat, depending on the history of the specific anode.

Figure 7 shows a simulation of the anode temperature close to the surface (5 cm) and the integral temperature. The anode is first cooled in a water bath with a mean temperature of 50°C for 1 hour and then air cooled (free convection).

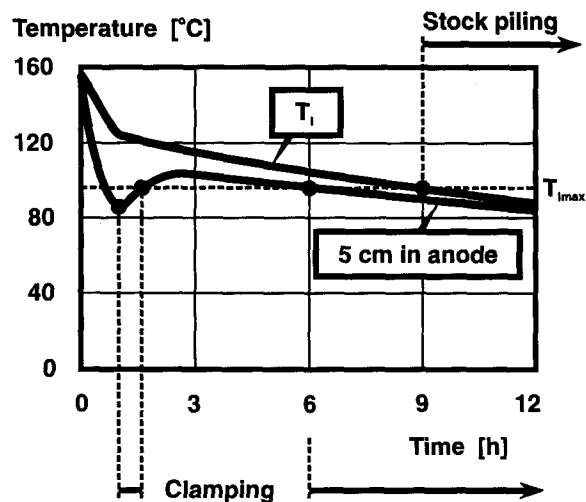


Figure 7: Integral temperature of a vibrated anode (1'000 kg, 1.6 x 0.7 x 0.6 m) cooled in a water bath (ø 50°C, 1 h) and subsequently by ambient air (25°C, free convection)

It is known by practical experience that with the given boundary conditions a green anode can be clamped right after 1 h of cooling in a water bath without damaging its surface. However, when the anode is clamped 1 to 2 hours after the main cooling, the surface can be damaged. This observation coincides with the results illustrated in figure 7.

The simulation shows that the temperature of the layer 5 cm inside the anode side surfaces reaches a minimum after one hour of water cooling. This minimum is below $T_{I_{max}}$. When the anode is removed from the water bath for further air cooling, the layer reheats within 30 minutes above $T_{I_{max}}$. It then takes 4.5 hours (i.e. 6 hours after forming) until the temperature of the 5 cm layer drops below $T_{I_{max}}$.

Based on the observations from practical experience and the results from the simulations, $T_{I_{max}}$ can be used as a criterion for the critical temperature 5 cm inside the anode side surfaces. The green anode can thus only be clamped without damaging its surface when this temperature is below $T_{I_{max}}$.

The evolution of the integral temperature T_I can be used as a criterion to define the conditions for stacking the green anodes for storage or baking. Figure 7 shows that it takes 9 hours (i.e. 1 hour water bath and 8 hours free air convection) until T_I reaches $T_{I_{max}}$. After this time the anode can be stacked without damaging its structure. When the anodes are transported directly to the bake furnace (without passing the storage area), it is possible to insert them into the pits earlier. However, packing material needs to be filled in instantly to stabilize the shape of the blocks.

Comparison of Pressed vs. Vibrated Anodes

Figure 8 shows that within one hour the crust of a vibrated anode can be cooled very efficiently in a water bath due to the high heat transfer coefficient. The limiting factor is the temperature conductivity of the material which causes the center to remain hot. As a consequence high temperature gradients result between the center and the surfaces. Due to the remaining heat in the center, the surfaces reach 100°C 3 hours after forming, which exceeds $T_{I_{max}}$.

Pressed anodes with a forming temperature of 110°C can be cooled without a water bath. Figure 8 shows a pressed anode that is cooled by an air blower (5 m/s) for one hour and then cooled by free air convection with an ambient temperature of 25°C. Due to the much lower temperature level, the stored heat in the center is not sufficient to reheat the surface above the critical $T_{I_{max}}$. Therefore, after one hour of cooling by forced air convection, the anode can be clamped without any restrictions.

Figure 9 compares the integral temperature of a vibrated and a pressed anode. The vibrated anode is cooled in a water bath for one hour with subsequent air cooling (free convection). The pressed anode is once cooled by free air convection for the entire duration and once by a blower (5m/s for 1h) followed by free air convection.

For the vibrated anode it takes 9 hours until the integral temperature T_I drops below $T_{I_{max}}$ and the anode can be stacked for storage. The pressed anode cooled purely in the ambient by free air convection

can be stored after 4.5 hours. With the air blower the pressed anode can already be stored after 30 minutes.

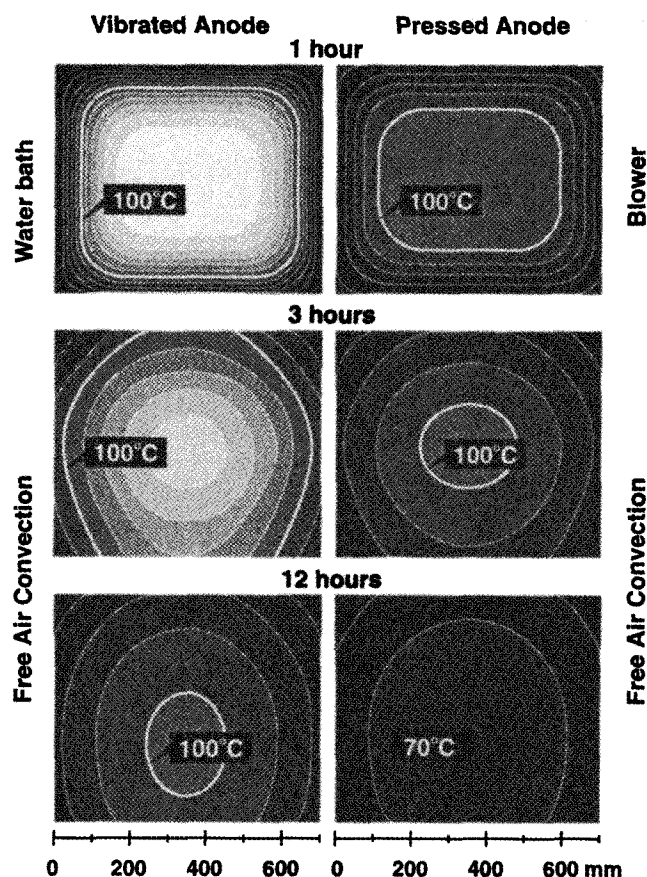


Figure 8: Isothermal lines with steps of 10°C in the vertical cross section for a vibrated anode (155°C) and a pressed anode (110°C). Anode size: 1.6 x 0.7 x 0.6 m

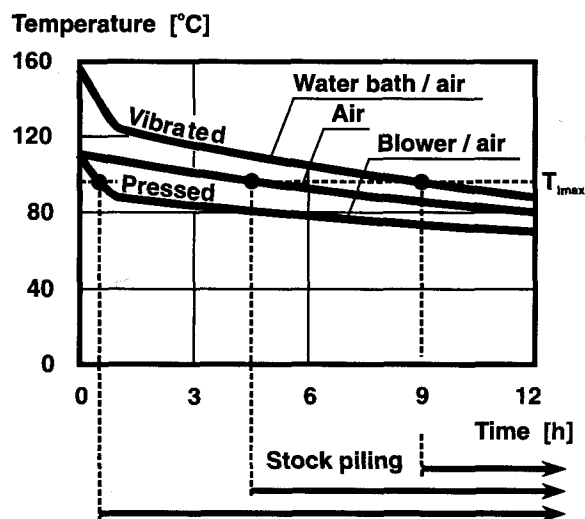


Figure 9: Integral temperature for a vibrated and a pressed anode determining the storage strategy

CONCLUSIONS

Based on the results obtained from the determination of the green anode properties, the temperature measurements and the computer simulations, the following conclusions can be drawn:

- The minimum cooling time required to avoid problems during handling, storage and subsequent processing is a function of the anode size and weight, the forming temperature and the type of cooling.
- The maximum integral temperature T_{Imax} of the anode can be used as a criterion to define the required conditions for handling and storage.
- Optimum cooling of vibrated anodes is achieved with a water bath operated using a counter current flow heat exchanger. The entrance water temperature for the anodes should be around 70°C.
- The use of a water spray instead of a water bath is less suitable due to higher investment and maintenance costs. Control of the jets to avoid thermal shock problems is difficult in particular for plant locations with extreme winter times.
- Pressed anodes can be cooled by the ambient air without a water bath. In case of very short transportation distances to the storage area or bake furnace, the installation of a blower reduces the required cooling time to 30 minutes.
- Green anodes can be clamped without damaging the surface when the temperature 5 cm inside from the surface is below T_{Imax} . For vibrated anodes this is the case directly after the water bath and again 5 hours later when the surface reheating has stopped. For pressed anodes the surface reheating occurs below T_{Imax} , therefore they can be handled anytime after the main cooling phase.
- Green anode can be stored in stacks without damage when their integral temperature is at least 10°C below the Mettler pitch softening point. Vibrated anodes cooled in a water bath for one hour can thus be stacked 9 hours after forming. Pressed anodes cooled in the ambient can be stacked after 4.5 hours, and combined air cooling with a blower reduces this time to 30 minutes.

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