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SALT RECOVERY FROM THE HOT TREATED ALUMINIUM MELTING DROSS RESIDUE

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Abstract: In the aluminium industry, the large amount of dross – a by-product of scrap melting – is usually further processed at high temperature re-melting to reclaim the high metallic content entrapped in material. The residue of the hot dross treatment is mainly composed of oxides, and chloride salts from the flux added during the thermo-mechanical process. The major NaCl and KCl components of the added salt are removed by a technically simple leaching process, however, the brine must be treated to remove the dissolved chlorides. We have investigated the energy requirement and efficiency of the evaporation procedure with a simple vessel of insulated walls and submerged heater. The specific heat capacity of the examined NaCl/KCl saturated solution of 2 : 1 mass ratio was determined as ~3155 J/kgK and the latent heat as 1538 J/kgK. The heat efficiency obtained with the system at room temperature initially was found to approach a 97% level as stable conditions were reached. The crystallized NaCl/KCl salt mixture – with possible modifications of it composition – can be recycled to the furnace.

Keywords: salt cake, salt removal, dross utilisation, evaporation

INTRODUCTION

The share of secondary raw materials used for aluminium production is continually increasing, however, melting scrap results in increased amount of dross produced [1, 2]. The heterogeneous structure of the dross may entrap a large amount of liquid metal [3, 4], which is usually recovered at the production site using thermo- mechanical "hot treatment". The re-melting treatment is carried out in an oxygen-gas fired rotary – "converter" – furnace where the added salt and the rotation helps to break the oxide layers surrounding the liquid metal droplets. The – usually NaCl-KCl based – salt is added in relatively large quantities (20–30%) to the treated primary dross. The residue of the thermo-mechanical treatment does not contain considerable metallic aluminium [5], therefore it is not feasible for further metallurgical processing, and is usually landfilled as hazardous waste. However different industries may be able to utilize, this by-product. In this case the "salt cake" residual dross must be further processed to eliminate certain harmful components such as the salt content [6]. The chloride salt is easily dissolved in water even at room temperatures, so it is practical to first treat the residue with a simple leaching procedure, earlier examined and optimised [7]. There are some commercial technologies offered for the water leaching of the salt cake,

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however the specific steps, and the process itself is usually confidential, and the efficiency of salt recovery is not disclosed.

To dissolve the salt content, it is practical to provide just enough solvent to achieve a saturated solution, which is ~24% salt content in water [7]. This is important for the redundant water can significantly increase the energy consumption of the evaporation process. It must be noted that the dissolution of NaCl and KCl is accompanied by a positive heat (+4 kJ/mol and 17 kJ/mol, respectively), thus the dissolution is an endothermic reaction, but the crystallization from the solution may generate some *in situ* heat to be utilized. After removing the traces of the adhering brine from the surface of the solid residue by washing and filtering, a salt free, mostly oxide material is obtained which can be used for various purposes [8, 9] however the concentrated salt solution must still be further processed.

The most practical way to eliminate the water content of the solution and to recover the salt is by evaporation. Various devices are widely available, [10] which are easy to operate even by waste heat available at the melting site. After the evaporation, the crystallized and dried salt can be recycled to the thermo- mechanical treatment of the aluminium melting dross after possible modification in the NaCl/KCl ratio.

1. EXPERIMENTAL PROCEDURE

In a previous study, [7] we have found that most of the salt content of the aluminium melting dross residue can be removed with a simple leaching step, applying water, followed by rinsing and filtering. However, to be able to recycle the salt to the hot treatment of the primary dross, the water content of the solution must be evaporated. The evaporation, while being a technically simple process, can be quite expensive because of the relatively high energy requirement. Therefore, we have started experimental investigations to clarify this practical aspect.

The concentrations of the different components in the solution influence the properties. The NaCl/KCl mass ratio in a saturated solution in equilibrium with the undissolved crystals is roughly ~2 : 1 (20.4 : 11.15) [11]. In view of these values some preliminary calculations could be carried out to determine the probable boiling point and specific heat capacity of the solutions by the following equations:

$$\Delta T_b = K_b * m_b * H \tag{1}$$

$$c_p = \sum_i \left(\frac{m_i}{m_t}\right) c_{pi} \tag{2}$$

Where: ΔT_b – boiling point elevation [°C,K],
K_b – ebullioscopic constant [K*kg/mol],
H – van 't Hoff factor,
cp – specific heat capacity of the solution [J/kg K]
i – the running index of the components,
m_i – dissolved amount of the indicated component kg,
m_t – total mass of the solution [kg].

The latter equation can provide an approximate result to verify the experimental results.

In practice, the efficiency considerations of recovering the chloride salt content of the aluminium melting dross is to use the least water possible during the leaching, which provides saturated solutions. Accordingly, the experiments were carried out with saturated solutions made by dissolving the (~ 63%NaCl ~32% KCl ~4%-CaF_2) flux – used in the industry for the hot processing of the dross – in distilled water. To ensure the desired concentration, the flux was added in excess. There are negligible (<1%) non-soluble contaminants in addition to the main components, therefore it is necessary to clean the solutions by filtering.

In order to determine the key properties influencing the evaporation process [12] of the solutions, an experimental device was set up, shown in *Figure 1*. The solution was poured in an insulated three-neck distilling flask. One of the openings was completely sealed. An immersion heater, which provided stable and measureable energy input was inserted in the main opening. The third neck was used to guide the water vapor to a condenser. The condensed water was collected in a beaker placed on a digital scale. The mass of precipitated salt and the overall volume loss could be calculated from the mass of the condensed water.

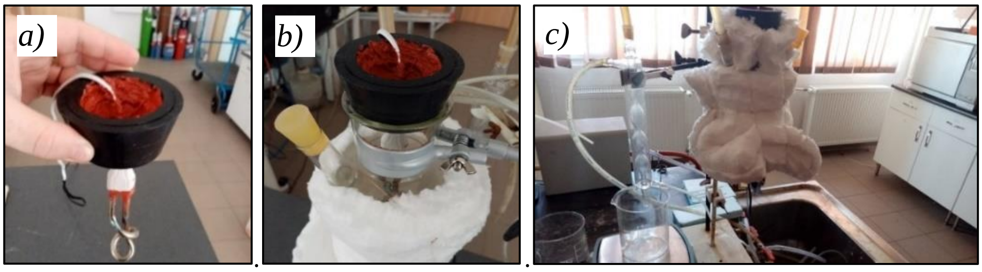

Figure 1
Immersion heater (a), insulated flask (b), the complete experimental setup (c)

The experiment was initially carried out with pure water to determine the practical deviation from the theoretically determined values. Each test lasted 9 minutes and was carried out with an initial volume of 500 cm^3, and the volume of the residual solution was measured after the procedure in a mess cylinder. The initial and final volumes, masses and temperatures were measured for water and the examined saturated salt solutions. The final solution was poured to a filter to remove the salt particles crystallized, and collected in a measuring cyllinder.

2. RESULTS AND DISCUSSION

The first task was to determine the deviation of the instrumentally measured energy consumption from that of the theoretically required value calculated from the collected mass and the physical properties of condensed water. These results can be seen on *Figure 2*.

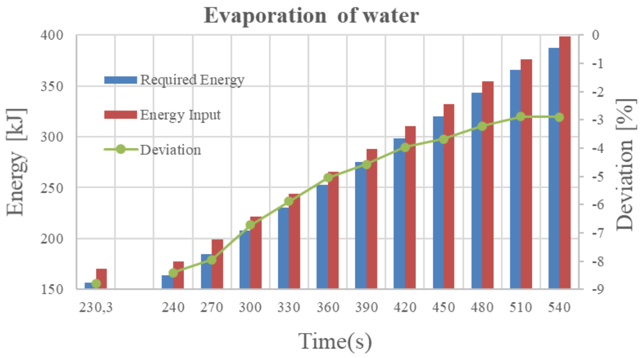

Figure 2
Result of the water evaporation experiment

The initial values at the first registered time represent the state when the solution just started to boil. Further points in time for data recording started at 240s continued with 30s intervals. The columns show the total energy measured directly by the electrical prameters and the theoretically required energy calculated from the measured mass of the condensed water. The points connected with a solid line represent the deviation of the practical energy input from the theoretical value relative to the theoretical energy requirement, expressed in percentages. Altough while reaching the boiling point the deviation was usually close to 9%, after 510 s it decreased, and was stabilized finally around 3%. The difference was due to energy loss needed to heat up the experimental system. The required energy during the evaporation of the salt solutions was calculated using this deviation.

To determine the salt content of the solution a rotary vacuum distiller was used. According to the results, 1 cm^3 of the solution contained 0.4 g salt, therefore the volume and mass loss could be related to 1 cm^3 of collected condensed water during the evaporation of the saturated salt solutions. The decrease in mass for the water and saturated salt solutions, respectively, and the theoretically required energy values are shown in *Figure 3*.

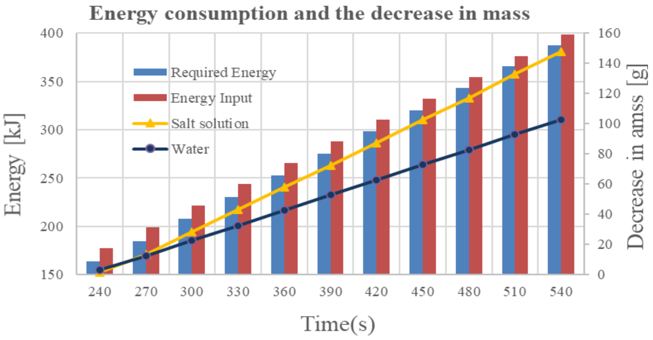

Figure 3

Results of the evaporation, comparing water and salt solutions

With the same energy input, the evaporated solution mass was ~1.5 times compared to that of water. The specific heat capacity of the saturated NaCl/KCl solution was calculated as ~3,155 J/kgK – which was quite close to the 3,117 J/kgK calculated with equation (6) – and the latent heat amounted to 1,538 J/kgK. With these values it was possible to make an approximate calculation to determine the energy consumption and necesarry time for the evaporation process. For this purpose the following equations were used:

Energy required to reach boiling point (Q_b, J):

$$Q_b = m \cdot c \cdot (T_{\mathrm{bp}} - T_i) \tag{3}$$

where: m – mass of the solution (kg),

c – specific heat capacity of the solution (J/kgK),

T_i and T_{bp} – initial temperature and the boiling point of the solution (K).

Energy required for evaporation:

$$Q_e = m \cdot L \tag{4}$$

Ahol m – evaporated mass (kg)

L – latent heat of evaporation of the salt solution (J/kg).

In the case of aqueous solutions the value of the latent heat is orders of magnitude higher than the heat required to heat the solution to the boiling temperature, therefore, the former can be considered as the dominant heat requirement. Another key parameter during the evaporation process is the heat transfer, which is highly influenced by the salt crystallized on the surface transferring the heat. In case of evaporating saturated salt solutions, an averege thickness of the salt layer (δ_{salt}) can be taken into account:
Thus the rate of heat flow (q, in Watts) :

$$q = \frac{1}{\frac{1}{\alpha_{\text{gas}}}+\frac{\delta_{\text{wall}}}{\lambda_{\text{wall}}}+\frac{\delta_{\text{salt}}}{\lambda_{\text{salt}}}+\frac{1}{\alpha_{\text{o}}}} \cdot A \cdot \Delta T \tag{5}$$

where: A – surface area of the heat transfer (m^2),
ΔT – difference between the internal and the external temperatures (K),
α_{gas} and α_{o} – heat transfer coefficents between the heating medium (gas) and the outside wall surface and the inside wall and the solution, respectively (W/m^2/K),
λ_{wall} and λ_{salt} – thermal conductivities of the vessel wall and the salt layer (W/mK),
δ_{wall} and δ_{salt} – avarege thicknesses of the vessel wall and the salt layer (m).

The total heat transfering surface is dependent on the size of the vessel used in the process. The volume of the solution must be considered for choosing the size of the vessel. This volume mainly depends on the amount of the dross residue, its salt content, and the volume of the water used in the leaching process.

The approximate energy, and time required to evaporate the solution of 1 m^3 volume could be calculated using *Equations (3–5)* and the characteristics of the saturated salt solution. Based on 1 m^3 inital volume and the vessel seen in *Figure 4*, assuming it is 1 m tall with a circular base surface of 0.5 m radius, the effective heat transfer surface is 4 m^2. In a general instanse of a heating furnace, the flue gas of ~230 °C can be used as a heating medium with.

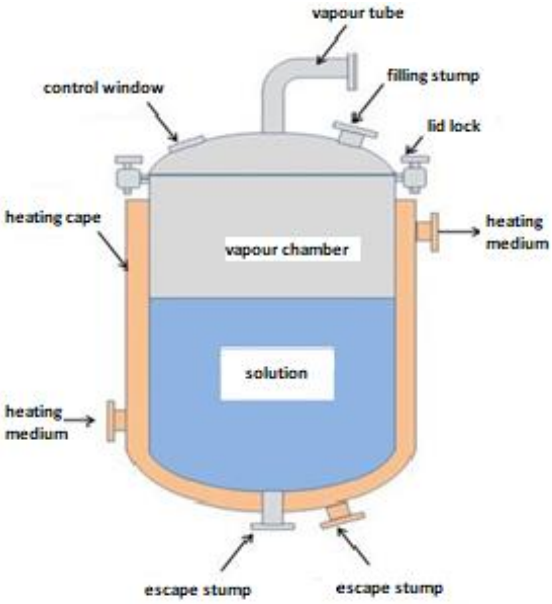

Figure 4
A standard batch evaporator device [10]

Additional physical [13] and technological paramaters are the following:

Averege temperature of the heating gas = 508 K
Material of the evaporator vessel: cast iron
Heat conductivity of cast iron: λ = 60,5 W/mK
Wall thickness: δ = 1 cm
Specific heat capacity of the saturated salt solution: c = 3155 J/kgK
Latent evaporation heat of the saturated salt solution: L = 1538 kJ/kg
Mass of the saturated salt solution: m = 1240 kg
Initial temperature of the saturated salt solution: 293 K
Heat conductivity of the salt layer: λ = 6,5 W/mK
Heat transfer coefficent of the heating medium: α_{gas} = 65 W/m^{2}K
Heat transfer coefficent of the heated medium: α_0 = 500 W/m^{2}K

1) Energy required to reach the boiling point (from 20 °C to 107.7 °C):

$$Q_b = c * m * \Delta T = 3155 \frac{\mathrm{J}}{\mathrm{kgK}} * 1240 \text{ kg} * 87 \text{ K} \cong \mathbf{340\ MJ}$$

2) Energy required for evaporation at atmospheric pressure:

$$Q = m \cdot L = 1240 \text{ kg} \cdot 1538 \frac{\mathrm{kJ}}{\mathrm{kg}} \cong \mathbf{1907\ MJ}$$

Therefore, to evaporate 1 m^3 solution, 2247 MJ energy input is required. This volume of the solution contains 400 kg of salt, which can form an avarege 4.8 cm thick layer over the surface of 4 m^2. However, the thickness of the salt layer is not constant over the cyllindrical surface. From the top (0 cm) the layer progressivly grows towards the bottom. Taking into account the ratio of the surfaces it can be assumed that an avarege of 6-7 cm salt layer is formed at the bottom, while an avarege of 3 cm thick layer can form at the side wall. Taking it into account, an overall avarege of 4 cm salt layer can be assumed by the end of the evaporation process. This value can be halved to express an average value referring to the entire processing time. Due to the decrease in the solution volume, the area of the effective heat transfer surface is gradually decreasing in the mean time from the initial 4 m^2 to a final approximately 1 m^2 near the bottom. Taking also the additional interior heat transfer into account, the effectice surface is considered approximately 3 m^2 for the entire length of the process. Therfore, the computation was based on a 1 cm thick cast iron wall with additional 2 cm thick salt layer the vessel – 1 m^3 capacity containing the 1240 kg solution – and applying 235 °C flue gas as heating medium and assuming ~110 °C internal temperature of the solution in boiling. With these values the energy transfered to the solution in 3,600 s can be expressed:

$$q = \frac{1}{\frac{1}{\alpha_{\mathrm{gas}}} + \frac{\delta_{\mathrm{wall}}}{\lambda_{\mathrm{wall}}} + \frac{\delta_{\mathrm{salt}}}{\lambda_{\mathrm{salt}}} + \frac{1}{\alpha_{\mathrm{o}}}} \cdot A \cdot \Delta T \cdot \tau = \frac{3.6 * 3 * 125 * 10^{-3}}{\frac{1}{65} + \frac{0{,}01}{60.5} + \frac{0{,}02}{6.5} + \frac{1}{500}} \cong 65.45\, {}^{MJ}\!/_{h}$$

At this rate, heating and evaporating 1 m^3 saturated salt solution takes (2247 MJ / 65.45 MJ/h) approximetly 34 hours.

If the crystallized salt is not removed and new batches of the soltion are treated in the same vessel, the increasing thickness of the salt layer is detrimental to the heat transfer. While without salt layer, the heat flux can reach 80 MJ/h, and with the the average 3 cm it can be

65.5 MJ/h, calculating with 6 cm thick salt layer it can drop below 50 MJ/h. The results of these effects are shown in *Figure 5*.

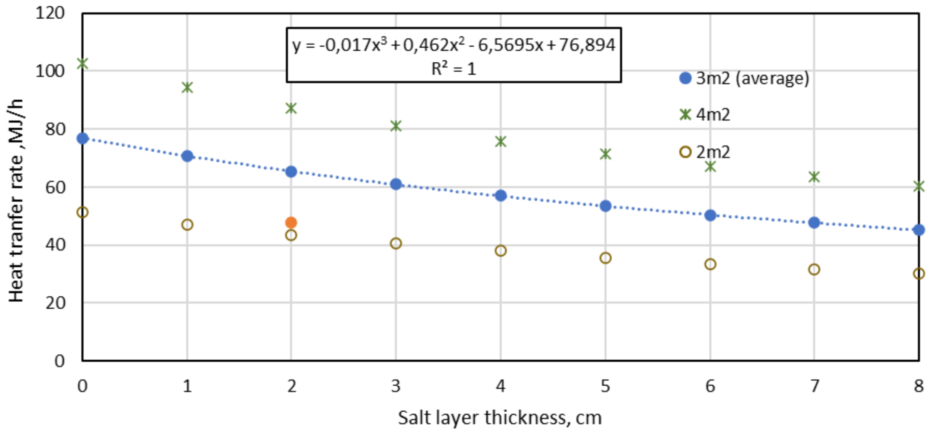

Figure 5

Heat transfer depending on the thickness of the salt layer (235 °C heating gas)

As a consequence, with thicker salt layers, longer time is needed for the evaporation. This is described by a linear correlation shown in *Figure 6*, assuming an even and avarege thickness of the salt layer, while evaporating 1 m^3 solution with different effective heat transfer surfaces and applying 235 °C flue gas as the heating medium.

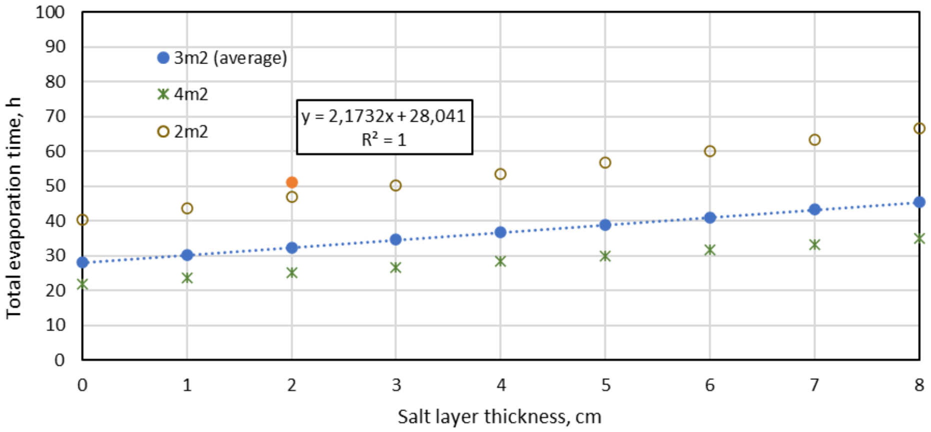

Figure 6

Total process time depending on the salt layer thickness and the effective heat transfer surface (1 m^3 solution, 235 °C heating gas temperature)

As there is less and less solution to evaporate with the progression of the process, the rate of heat transfer is constantly decreasing, slowing the whole process. To achieve a more intensive heat transfer, it is most practical to increase the temperature of the heating gas. Even increasing it by 100 °C, a significant improvement can be achived, as shown in *Figure 7*.

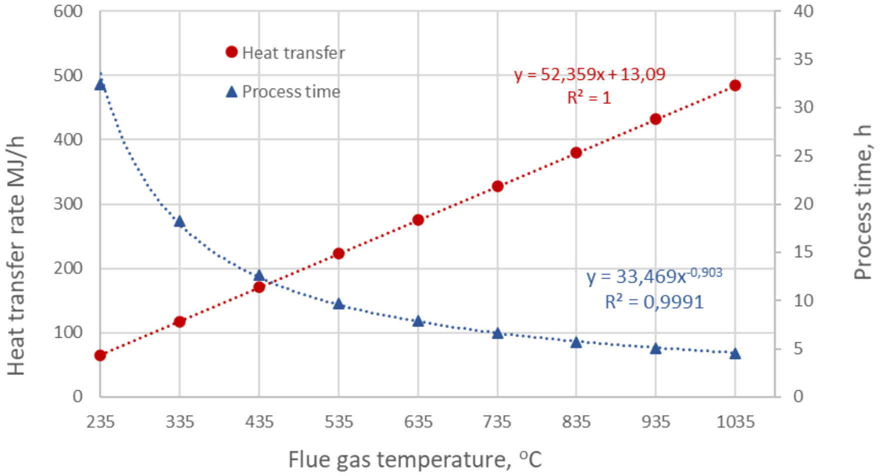

Figure 7

Achievable heat transfer rate during the heating and evaporation process, and the process time depening on the flue gas temperature

A rise of 100 °C from the basic 235 °C gas temperature can already halve the time required for the complete evaporation, this way, especially with thicker salt layers it can be of key importance. It may be taken into consideration to include a burner to supply some secondary heat and elevate the gas temperature. The total required times of evaporation with different thicknesses of salt layers is shown as a function of the gas temperature in *Figure 8.*

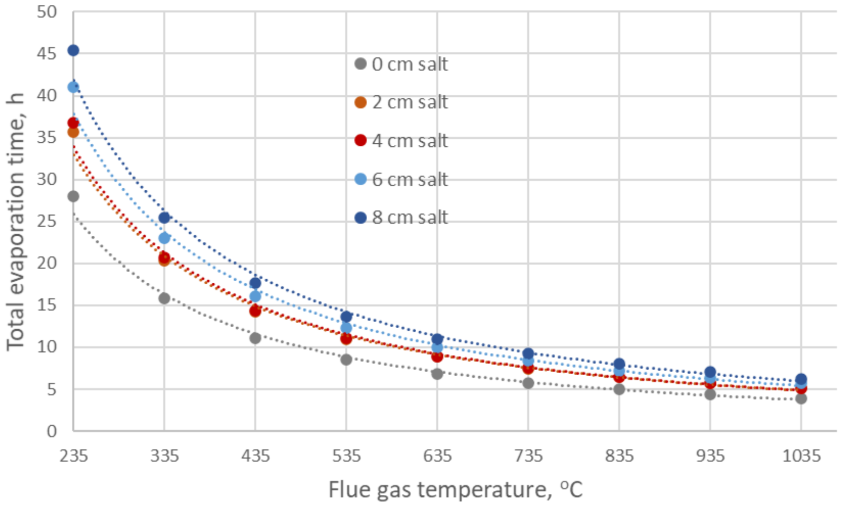

Figure 8

Total process time as a function of the heating gas temperature with different salt layer thicknesses

CONCLUSIONS

Large amounts of dross are formed in aluminium melting, when using secondary raw materials with varying shapes, sizes, and origins. A part of the metal lost during the melting process can be recovered with the hot treatment of the dross applying considerable amounts of added salts. The residual dross of high chloride salt content is usually disposed of as hazardous waste. Removing the KCl-NaCl content of the residue may be beneficial economically and environmentally because the material after the leaching process is mostly made of oxides, thus it can be used as a raw material in other industries.

The removal of the salt components can be achieved with a straightforward leaching treatment, which results – ideally – in saturated solutions. Evaporating these solutions allows the recycling of the salt to the hot dross processing technology. The most crucial part of the evaporation process is the energy requirement. By measuring the energy needed and calculating the heat transfer – considering the potential salt formation during evaporation – the efficiency and process time could be determined. Increasing the temperature of the off-gas – obtained for example from the hot dross treatment – even by 100 °C, the process time of the evaporation can be halved.

Evaporating in multiple steps may be another solution. In one step part of the water content can be evaporated. After removing the salt previously crystallized on the evaporator walls, the process can be continued with intensive stirring which obstructs the formation of a solid salt layer. The salt then can be settled and removed. This final salt – with minimal water content – may be recycled to the dross processing rotary furnace during its heating phase where the rest of the moisture content can leave the system.

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