# Two-Stage Pot Gas Treatment Technology Allowing the Production of Sodium Sulfate

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## Abstract

The key task of any socially responsible entity is to protect the environment from harmful effects of plant operation. UC RUSAL has developed and implemented at RUSAL Krasnoyarsk a two-stage pot gas treatment technology allowing the production of sodium sulfate, ensuring maximum efficiency in entrapping pollutants (dust, fluorides, and sulfur dioxide) and eliminating the need to build new landfills. Therefore, the important environmental task facing the plant has been solved. This paper describes the key process and technical aspects of the above technology. The first step includes the process of adsorbing fluorides and dust from the gas. The second step includes the process of adsorbing sulfur dioxide and the additional removal of the remaining fluorides and dust; and the third step includes the removal of sulfur, in the form of sodium sulfate, from the closed wet scrubber (WS) liquor circulation loop to increase the efficiency of the second gas treating step and eliminate the need to build new landfills. The resulting sodium sulfate can be used as a commercial product in paper pulp production.

**Keywords:** Pot gas treatment, dry scrubber, wet scrubber, sodium sulfate.

## 1. Introduction

Modern history of Krasnoyarsk Aluminum Smelter (KrAZ) includes a series of milestones to improve environmental situation, rationalize and upgrade existing environmental protection technologies. To improve systems cleaning cell off gases is among such significant milestones. Traditionally, smelters in the Soviet Union were equipped with two-stage gas treatment systems: Stage 1 – electrical filter to clean dust and tars, Stage 2 – wet scrubbing to remove fluorine, sulfur compounds, additional cleaning from dust and tars and discharge of saturated solutions to the settling ponds. Under modern conditions such a scrubbing system fails to meet treatment efficiency requirements.

The first stage of upgrading KrAZ gas scrubbing equipment was to completely replace all electric filters for up-to-date dry gas scrubbers with the operating principle based on screening the pollutants by alumina adsorption. Dry gas scrubbers reduced emissions of gaseous and solid fluorides, inorganic dust by 40 %, benz(a)pyrene and tars – by 15 %.

The second stage of wet gas scrubbing is to capture sulfur dioxide. Until recently the essential fault of the existing two-stage gas scrubbing at Krasnoyarsk Aluminum Smelter was the necessity to use settling ponds to discharge solutions saturated with sodium sulfate and, as a consequence – closed water turnover – accumulation of sodium sulfate. High concentrations of crystallizable sodium sulfate reduce efficiency of gas scrubbing equipment and necessitate its frequent maintenance and cleaning. Among possible solutions of this problem is to dilute sodium sulfate with industrial water to reduce its concentration; this, however turns up another ecological challenge – restricted volume of existing ponds and the need to build new ones.

For the period of 2015 - 2017 specialists of RUSAL ETC LLC improved the existing two-stage gas scrubbing process. Up-to-date process meeting requirements of environmental laws and regulations, ensuring maximum achievable at the current technological horizon efficiency of gas treatment with closed solution turnover and production of dry sodium sulfate in demand in the market has been developed and implemented.

## 2. State-of-the art Gas Scrubbing Processes in Aluminum Production

All currently known methods of arranging fume gas treatment processes can be divided into cyclic and noncyclic; the cleaning process as it is classified as follows: adsorption, absorption and chemisorption (Figure 1).

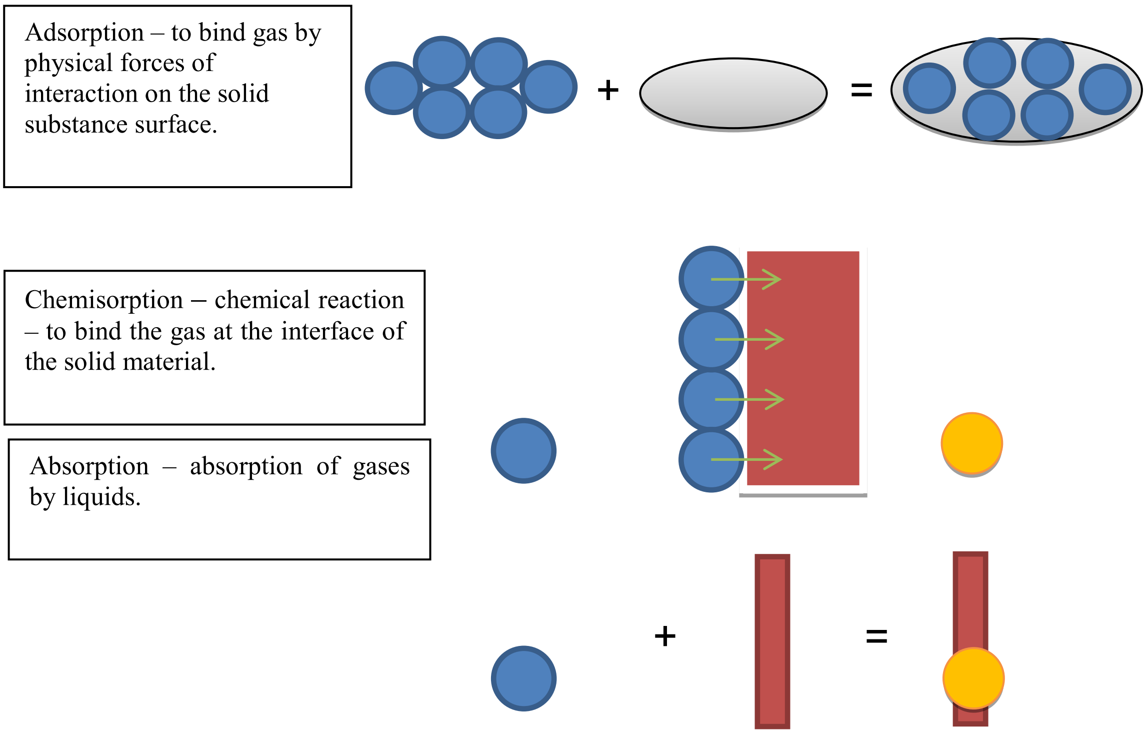



**Figure 1. Methods of gas treatment.**

In industrial enterprises gas treatment is broken up into 3 main groups by pollutant capturing method: Gas phase (dry) method, Liquid phase (wet) and Combined (wet-dry method).

### 2.1. International Practices

In actual practice most widespread are combined gas scrubbing units employing «dry» + «wet» or «dry» + «wet-dry» methods at different treatment stages. For the aluminum industry two stages of gas treatment in addition to industrial gas cleaning make possible to achieve savings on expendable materials, as after the 1$^{st}$ treatment stage expensive fluorine compounds are again delivered to the electrolysis process. The cell gases are, at that, successfully, cleaned from fluorine compounds and solids – dust particles - up to 99.9 %. The second treatment stage is to remove residual fluorine compounds and capture gaseous sulphurous (sulfur) anhydride followed by discharge of sulfate compounds to the settling ponds or by production of commercial gypsum.

The absorbent for the «wet» treatment method is industrial or sea water. This technique makes possible to substantially reduce negative impact of production on the aerial environment of the territory. An example of two-stage gas treatment at an aluminum smelter is QATALUM (Qatar) (Figure 2), located onshore and using sea water to clean the pollutants.

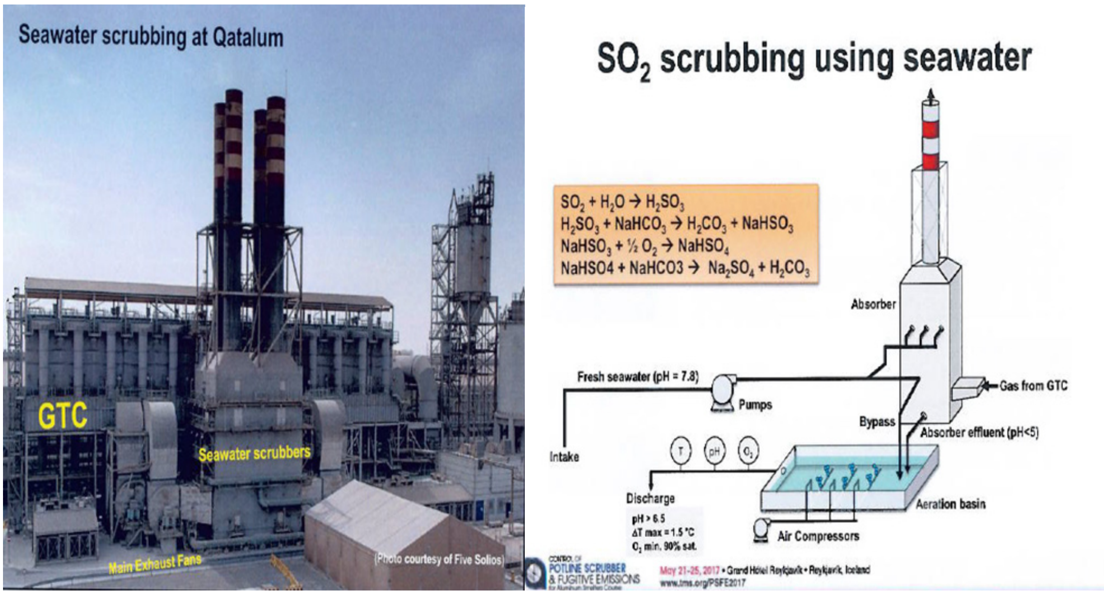



**Figure 2. Qatar Aluminum Smelter.**

As of today the «wet» scrubbing is primary process in aluminum smelter over the globe because of its efficiency and low price of the primary production, however this method is not always possible for the lack of a sea or territory to place settling ponds. Global aluminum producers employing two-stage gas scrubbing are presented in Table 1.

**Table 1. Global aluminum producers employing two-stage gas scrubbing.**

| Smelter | Stages | | Disposal | Supplier |
|---|---|---|---|---|
| | Stage 1: HF | Stage 2: SO2 | | |
| Mesaieed/Qatalum | Dry gas scrubbing | Wet scrubber (reactant - sea water) | Ocean | Five Solios |
| Taweelah/EGA 1-2 | Dry gas scrubbing | Wet scrubber (reactant - sea water) | | GE (Alstom) |
| Arvida/Rio Tinto | | Wet scrubber (reactant - soda ash) | Ocean | n/a |
| Massena (East) | Dry gas scrubbing | Wet scrubber ( reactant - soda ash ) | Ocean | n/a |
| Mosjoen/Alcoa | Dry gas scrubbing | | Ocean | Alcoa |
| Karmoy/Haas | Dry gas scrubbing | | Ocean | ABB Environmantal (Flakt) |
| SORAL | Dry gas scrubbing | | Ocean | ABB Environmantal (Flakt) |
| ElkemLista/Alcoa | Dry gas scrubbing | Wet scrubber (reactant - sea water) | Ocean | ABB Environmantal (Flakt) |
| Aardal/Haas | Dry gas scrubbing | Wet scrubber ( reactant - soda ash ) | Ocean | ABB Environmantal (Flakt) |

| | | | | |
|---|---|---|---|---|
| Hoyanger/Haas | Dry gas scrubbing | | Ocean | ABB Environmantal (Flakt) |
| Sunndalsora/Haas | El. filter + dry gas scrubbing | | Ocean | ABB Environmantal (Flakt) |

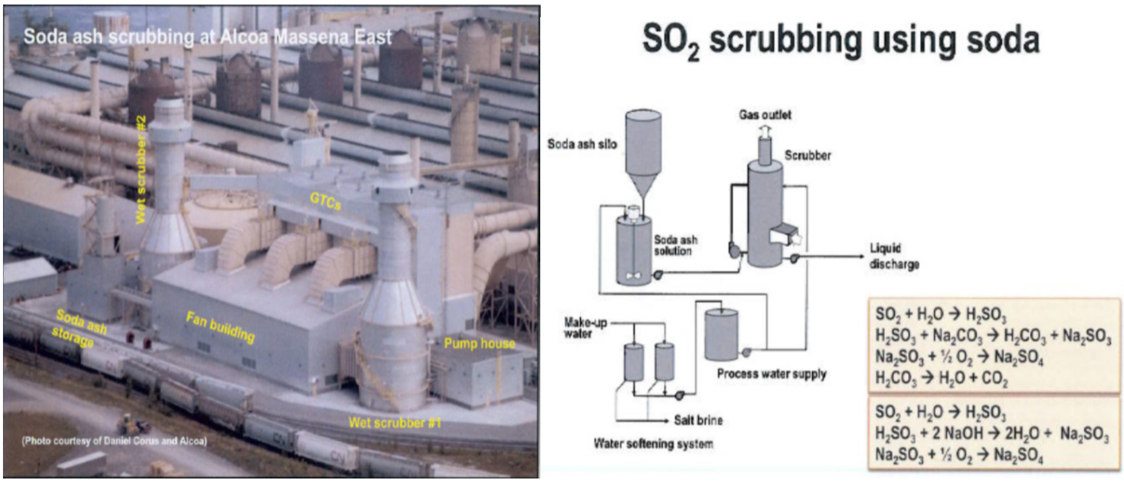



**Figure 3. Wet stage at Alcoa aluminum smelter.**

A way out of this situation is to use «wet-dry» method as the second cleaning stage. The advantage of this method is to produce instead of waste a commercial product in the form of dry industrial gypsum used as a cementing material in concrete production. Currently Alcoa Company is performing industrial tests of this process at LakeCharles smelter, LA.

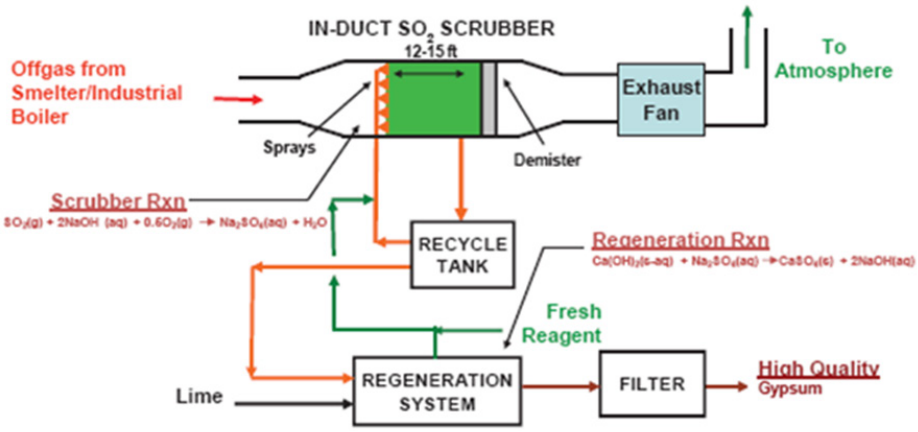



**Figure 3a. Alcoa flow diagram of gas treatment.**

The prospect of producing commercial product in the form of industrial gypsum is very expedient, specifically for the countries experiencing shortage of construction materials. This also makes possible to decrease substantially the cost of cleaning industrial gases in aluminum industry [1].

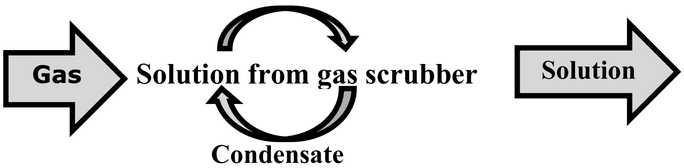
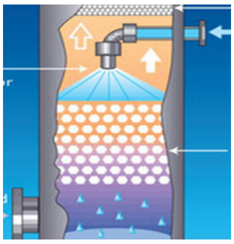
## 2.2. RUSAL Experience

Potrooms of Krasnoyarsk Aluminum Smelter are equipped with two-stage gas scrubbing. The first stage employs gas scrubbers designed by Alstom, RUSAL VAMI and Procedair operating by conventional reactor-filter scheme. The second gas scrubbing stage employs foam apparatus and hollow scrubbers functioning as absorbers of gaseous sulfur dioxide and absorbers of dust and tars. Gas is cleaned by interaction with sodium bicarbonate solution:

Na2CO3 + HF →NaF + NaHCO3 (1)
NaHCO3 + HF →NaF + CO2 + H2O (2)
Na2CO3 + CO2 + H2O →2 NaHCO3 (3)
Na2CO3 + SO2 + 0,5O2 →Na2SO4 + CO2 (4)

For the third stage a process to remove sodium sulfate from gas scrubber solutions has been developed. Table 2 shows stages of treating cell off gases removing sodium sulfate and efficiency of each process.

**Table 2. Two-stage gas scrubbing and sodium sulfate production.**

| **Two-stage gas scrubbing and sodium sulfate production** | | | |
|---|---|---|---|
| RUSAL dry gas scrubbing | Wet gas scrubber with closed-loop water turnover | Evaporation plant | Centrifuge |
|   | | | |
|  |  |  |  |
| Removal of dust, fluorine, tars **EFFICIENCY > 99.0 %** | Removal of sulfur **EFFICIENCY > 96.7 %** | Removal of sulfur from gas scrubbing solutions as dry sodium sulfate. **Closed cycle** | |

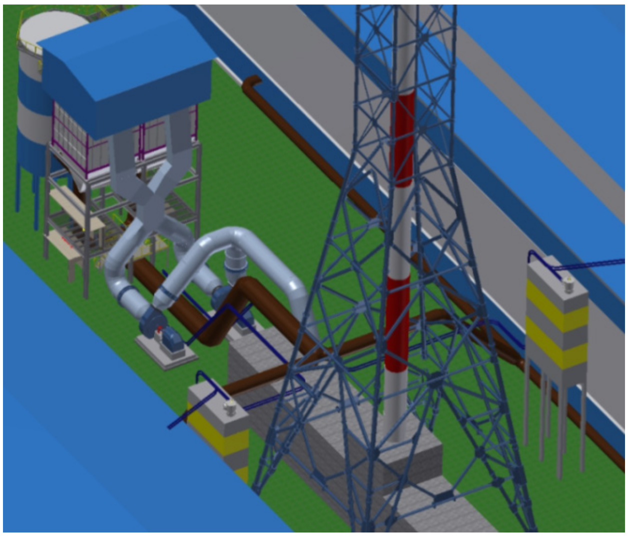


**Figure 4. RUSAL gas treatment diagram.**

## 3. Removal of Sodium Sulfate from RUSAL Gas Treatment System

The second stage cleaning employing soda ash captures sulphurous anhydride and in the presence of oxygen it oxidizes to sodium sulfate according to reaction (4). In this way the gas scrubbing solutions accumulate sodium sulfate. Accumulation of sulfates in gas scrubbing solutions leads to several negative consequences. First of all, solubility of sodium fluoride decreases and the solutions get oversaturated. This forms salt deposits on the equipment, results in fluorine and soda loss, increase of fluorine discharge to the settling ponds, overfilling of the settling ponds.

Besides, the regeneration cryolite contains up to 12% sodium sulfate because of sulfate co-deposition in cryolite formation. Together with sulfate the regeneration cryolite enters the aluminum electrolysis process.

In the presence of metal and carbon the sodium sulfate enters the cell to react with the bath and take part in redox processes and in the form of $SO_2$ is emitted with the gases. In the bath the following reactions proceed:

$$3Na_2SO_4 + 2Na_3AlF_6 \leftrightarrow Al_2(SO_4)_3 + 12NaF \quad (5)$$
$$Al_2(SO_4)_3 + 3e \leftrightarrow Al_2O_3 + 3SO_2 + 3CO \quad (6)$$
$$3Na_2SO_4 + 8Al \leftrightarrow 3Na_2S + 4Al_2O_3 \quad (7)$$
$$S_{2-} - 2e = S \quad S + 2CO_2 = SO_2 + 2CO \quad (8)$$

Exchange reaction (5) increases cryolite ratio of the bath and to correct it requires additional aluminum fluoride. Sulfates dissolved in the bath are recovered by the metal and carbon – this involves additional expenses of electric power to re-recover aluminum from $Al_2O_3$.

Besides, S content in the bath more than 0.02 % S drastically deteriorates bath performance. Therefore the necessity to remove sulfates from gas scrubbing solution is obvious.

### 3.1. Laboratory Studies to Remove Sodium Sulfate

As applied to gas scrubbing conditions at Krasnoyarsk Aluminum Smelter removal of sulfates from solution is possible in several ways. Among the simplest is to evaporate the solution after gas treatment followed by separation of the salt gel. After separation of the gel the mother liquor is returned from the gas scrubbing unit. When solution is evaporated after gas scrubbing bicarbonate decomposes according to reaction:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (9)$$

to produce soda-sulfate-fluorine solution. Neglecting presence of NaF in the solution, the behavior of the solution meets $Na_2SO_4$- $Na_2CO_3$ - $H_2O$ system which is well understood and well presented in the reference literature. The isotherm of this system at 75 °C is shown in Figure 5.

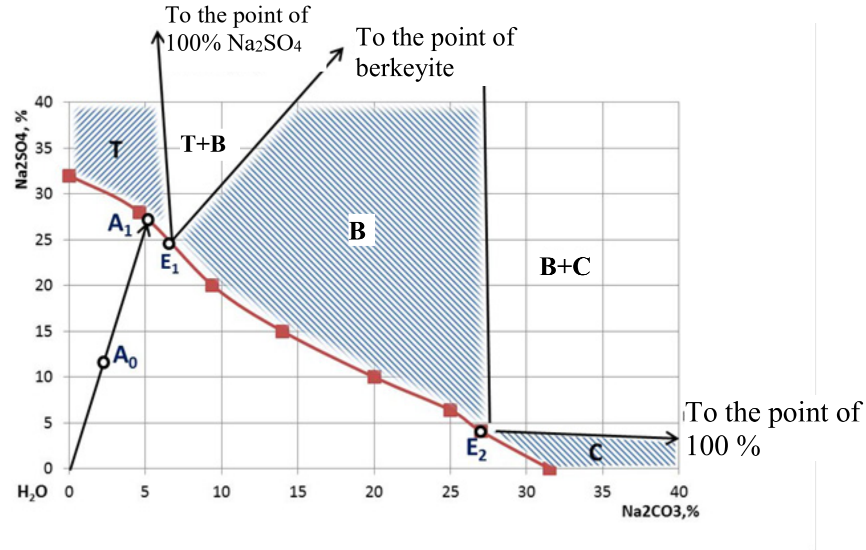



**Figure 5. Isotherm of $Na_2SO_4$-$Na_2CO_3$-$H_2O$ system at 75 °C.**

The water corner of the diagram in Fig. 5 corresponds to the compositions of saturated solutions which achieve saturation at isotherm line E1 - E 2. Above the isotherm are the salt crystallization fields, namely: in T field – tenardite (anhydrous $Na_2SO_4$), in B field – berkeyite (binary salt $2Na_2SO_4{\cdot}Na_2CO_3$) and in C field – soda (anhydrous or monohydrate depending on the temperature). Fields of joint crystallization of sulfate with berkeyite, and berkeyite with soda are in the intermediate sectors between the said fields.

In this presentation the composition of initial system after gas scrubbing is in imaging point A0. From the position of this point it is apparent that the solution is nonsaturated. Its evaporation will move point A0 by evaporation path to point A1, located on line E1 – E2. The ratio of lengths of A○ - $H_2O$ and A○ – A1 segments indicates that the saturation condition is achieved in double evaporation of the initial solution in terms of volume. Besides, from diagram in Fig. 5 it can be seen that the point of composition A1 is close to eutonic point E1. This means that the composition of the sediment by proportion of $Na_2SO_4$ / $Na_2CO_3$ salts will be approximately similar to that in the initial solution. Enrichment of the sediment with sulfate can be expected only with considerable decrease of soda and bicarbonate in the initial solution. After evaporation to saturation condition the solution should be evaporated 2 – 3 times to sediment main part of the sulfate. E.g. if the initial solution with $Na_2SO_4$ = 150 - 160 g/L is evaporated four times at 20 $m^3$/h, then with residual sulfate concentration at the level of 350 g/L the amount of extracted $Na_2SO_4$ will be about 1.2 t/h. Consequently, to increase sulfate removal it is necessary to increase either the flow of initial solution or the evaporation depth.

So, analysis of behavior of salt system $Na_2SO_4$ - $Na_2CO_3$ - $NaHCO_3$-NaF - $H_2O$ shows, that evaporation of the recycled solution after gas scrubbing makes possible to remove the sulfate from the process; however, given the existing composition of the solution it is expected to receive sulfate sediment containing soda and sodium fluoride in approximately the same proportion as in the initial solution. In the case of evaporation of the initial solution with lower soda and bicarbonate content and/or higher sulfate content sulfate enrichment of the sediment can be expected. To verify these theoretical considerations we carried out laboratory experiments.

Experiments to evaporate solutions were carried out in the laboratory evaporation plant. The evaporation process was carried out in a steel container heated on electric hot plate with controlled heating. To prevent clogging of the container bottom with scales the solution was agitated with a stirrer, the stirrer shaft passed through a stuffing box in the evaporator-container cover. Vapor from the evaporator was fed into separator where it was cleaned from foam and solution splashes. Treated vapor from the separator condensed in the cooler, the cooler coil was sprayed with cold water. The quantity of produced condensate was measured with measuring cylinder. When required depth of evaporation was achieved the slurry from the container was filtered from the sediment. Weight and moisture content of the sediment, volume and density of the filtrate were evaluated. Solutions and sediments were analyzed for $Na_2O$ т, $Na_2SO_4$, $Na_2CO_3$, $NaHCO_3$ and NaF.

Laboratory studies showed that on the whole the behavior of evaporated solution follows the regularities of particular system $Na_2SO_4$- $Na_2CO_3$ - $H_2O$ with the following specifics:

- Sodium fluoride is extracted from the solution with first sediment doses, when the evaporation depth increases NaF content in the sediment decreases;
- .Under laboratory evaporation conditions (atmospheric pressure and at temperature 102-104 °C) bicarbonate $NaHCO_3$ decomposes incompletely, as a result $Na_2CO_3$ settling in the sediment increases with evaporation depth.

## 3.2. Methods of Cleaning Sodium Sulfate from Fluorine Compounds

In literature different methods of purifying solutions containing fluorine compounds are considered. We turn our attention to basic sources:

- Calcium containing reactant (calcium hydrate).
  However, in our studies we failed to settle fluorine to a sufficient degree. The reason is that in alkaline solution is precipitated by lime only partially.
- Acid salt of aluminum sulfate.
  This salt interacts with fluorine compounds selectively. After the gas scrubbing solution interacts with aluminum sulfate the filtrate consists of sodium sulfate solution, while fluorine settles in the form of $Na_3AlF_6$.
- Cryolite production.
  The recycled solution is fed to produce secondary cryolite, after separation of cryolity the mother liquor is divided into parts, one of which is returned to gas scrubbing, and the other – to evaporation.

## 4. Sodium Sulfate Removal Flow Chart

The initial nonsaturated salt solution enters the evaporator (Figure 6). In the evaporator this flow joins the solution flow circulating inside the apparatus in closed loop. The solution flow is circulated by axial circulating pump which is part of the evaporator. In the evaporator the total flow of initial salt solution and circulating evaporated solution boil. The boiling process proceeds under vacuum by heat supplied through heat exchanging pipes with heating steam condensing in the heating chamber. When the solution boils secondary steam is released and the solution is concentrating (increasing density). To increase heat transfer during condensation of the heating steam entering the heating chamber of the evaporator and decrease its temperature the condensate is injected into the overheated steam. After the boiling process the evaporated solution from the evaporator drains by gravity into the receiving tank. From the tank the solution is cyclically pumped from the apparatus.

The secondary steam forming in the evaporator during boiling of the solution is directed to the barometric-capacity condenser. In the condenser the steam contacts with cooling clarified water supplied from the settling field to condense. The noncondensing gases and noncondensed water steam forming the vapor-gas mixture from the condenser are fed into the vacuum pump. The pump generates primary vacuum in the unit and maintains it during operation. The heated cooling water and the secondary steam condensate drain through the barometric pipe by gravity into hydraulic lock tank and further on to the pump. This pump removes the cooling water and condensate flow from the unit.

The product produced is centrifuged or filtered with subsequent drying to be stored and delivered to the consumer.

The advantage of the unit is the use of excessive during warm season process steam produced by the carbon plant. The evaporator makes possible to:
- Reduce $Na_2SO_4$ concentration in gas scrubbing solutions;
- Withdraw from construction of new settling ponds;
- Reduce idle time to clean the «wet» stage to improve efficiency of gas scrubbing facilities;
- Exclude recycled water to dilute solutions supplied to gas scrubbing;
- Evaporate gas scrubbing solutions at the rate not less than 10 $m^3$/h;
- Remove not less than 2.4 t/h of concentrated sodium sulfate solution with concentration not less than 200 g/L.

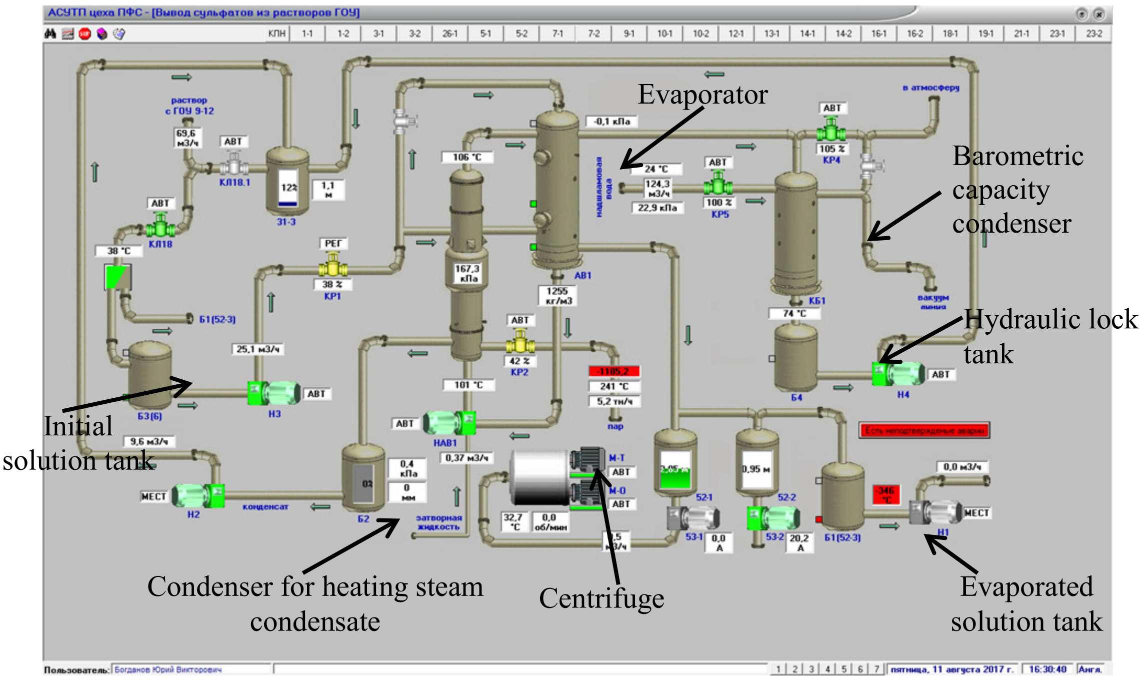



**Figure 6. Process flow diagram of sodium sulfate removal area**.

### 4.1. Technology Performance Data of Evaporator

The evaporator was put into continuous operation in May 2017. Up to date all process procedures providing for its stable operation have been fine tuned. More than 50 tons of dry sodium sulfate has been produced. Basic performance data of the evaporator are presented in Table 3.

**Table 3. Basic performance data of the evaporator.**

| Index | Units of measurement | Value |
|---|---|---|
| Productivity:<br>- initial solution<br>- evaporated water | <br>$m^3$/hour<br>kg/h | <br>20 - 25<br>10 000 - 12 000 |
| Heating team mass flow | kg/h | 5000 - 6000 |
| Heating steam pressure in the evaporator (absolute) | MPa | 0.12 – 0.23 |
| Heating steam temperature | °C | 250 - 270 |
| Input temperature at the evaporator | °C | 100 - 101 |
| Output temperature at the evaporator | °C | 105 - 106 |
| Evaporated solution density | kg/$m^3$ | 1260 - 1380 |
| Volume consumption of cooling overslurry water | $m^3$/h | 100 - 120 |
| Rated output power of the pump | kW | 150,5 |
| Operation mode – continuous | Hours per day | 24 |
| Number of working days per year | | 300 |
| Number of shifts per day | | 2 |

## 5. Conclusions

Removal of removing sodium sulfate accumulated in gas scrubbing solutions by evaporator was improved specifically: Dehydration is performed by centrifugation, ready product is dried in rack driers. The produced sodium sulfate contains 85 - 87 % of sodium sulfate, 8 – 10 % of sodium fluoride and some amount of soda and sodium bicarbonate.

As the demand for this product by main consumers – producers of cellulose, detergents, binding additive for production of copper, mud additives fluorine increases – the removal process has been developed and implemented.

As of today the scrubbing process is undergoing pilot tests. Pilot lot of 60 t of purified sodium sulfate is built up to conduct tests at Bratsk pulp-and-mill combine. After removal of fluorine the sodium sulfate will contain more than 95 - 97 % of primary product.

Thus, a serious ecological problem, associated with the necessity of building new settling ponds, has been solved, operation efficiency of gas scrubbing equipment has been increased, expenses to maintain it have been decreased.

## 6. Acknowledgement

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## 7. References

1 TMS Control of Potline Scrubber & Fugitive Emissions for Aluminum Smelters Course, www.tms.org/PSFE2017.