

New Products from Sulphate Producing Wet Scrubbers in Aluminium Reduction

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Abstract

Due to increasingly high sulphur content in carbon materials for electrolysis and using fuel oil for calcination of alumina, more and more smelters equip their gas cleaning facilities with wet scrubbing for catching sulphur compounds. The wet scrubbing processes used in aluminium reduction produces a liquid discharge containing fluorine and sulphur compounds, coal dust, etc. Due to increasing contents of said compounds, these solutions should be disposed to the tailing retention dyke suitable for liquids of a high class of hazard. A technology of processing the wet scrubbing liquid discharge was developed to produce recycled cryolite, soda solution for gas scrubbers and a soda-sulphate mixture. Said mixture contains $\geq 95\%$ burkeite $\text{Na}_2\text{CO}_3 \times 2\text{Na}_2\text{SO}_4$ and has excellent is characterised by its colour which indicates its quality. Soda-sulphate mixture is widely used in production of synthetic detergents and cellulose and paper. A pilot facility was built in the Krasnoyarsk aluminium smelter to test the suggested technology. Scaling up of the facility allows preventing the extension of tailing disposal areas of aluminium smelters. The pilot facility produces the soda-sulphate mixture of $> 80\%$ whiteness. Jointly with a chemical works, detergent production was established resulting in successful solution of the problem.

Keywords: Wet scrubbing, Soda sulphate mixture, Detergent, Whiteness.

1. Context and Present Situation

RUSAL's aluminium smelters use a two-stage gas treatment system, which allows cleaning potline gases from dust, HF hydrogen fluoride and SO_2 . The hydrogen fluoride adsorbed on alumina is returned as a raw material to electrolysis. The sulphur dioxide adsorbed by the soda solution is converted to sodium sulphate and pumped to the tailing retention dyke for clarification through precipitation of sodium sulphate salts and available coal dust particles.

The constant generation of soda-sulphate solutions results in a number of problems:

- At closed water circulation, sodium sulphate accumulates in solutions resulting in salt precipitation in the pipelines and gas treatment equipment. This adversely impacts the performance of the gas treatment equipment; and
- The accumulation of sodium sulphate in tailing dykes at RUSAL's aluminium smelters increases the area of the dykes as well as charges for waste disposal, moreover, it causes environmental problems.

RUSAL adopted a programme to find a solution to avoid the accumulation of sodium sulphate by producing a marketable product from it instead.

A study on the sodium sulphate market showed that its main consumers are as follows (Figure 1):

- Detergent production
- Pulp and paper industry

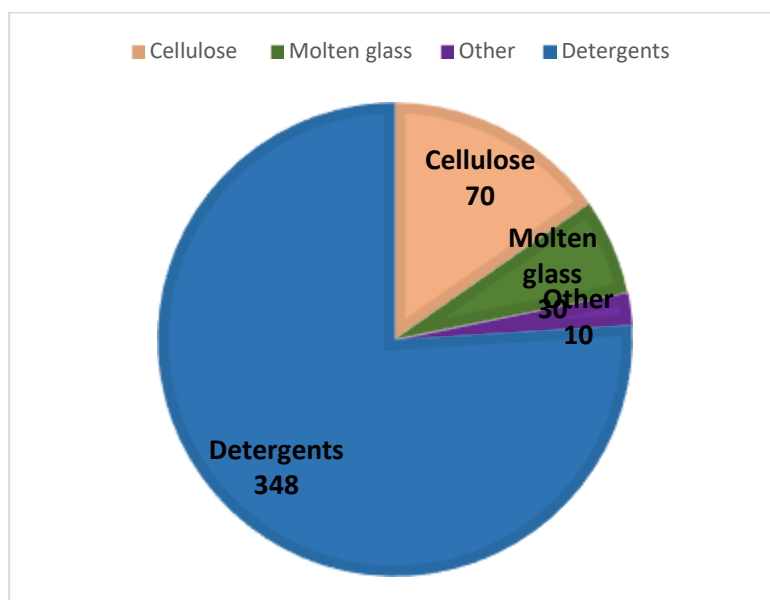


Figure 1. Sodium sulphate consumption, thousand t/a.

For these consumers, some of the priority properties of sodium sulphate are as follows:

- High whiteness;
- Stable quality with minimal impurities, including fluorine compounds;
- Market analysis has shown that consumers would prefer to purchase a soda-sulphate mixture instead of sodium sulphate, as the mixture shows better performance.

In 2014, Krasnoyarsk Aluminium Smelter (hereinafter referred to as KrAZ) installed the first pilot facility for evaporation of spent solutions from gas treatment centres (hereinafter referred to as GTC solutions) and separation of sodium sulphate in form of a solid salt with the following composition:

- 75 ÷ 80 % of sodium sulphate Na_2SO_4 ;
- 20 ÷ 25 % double salt with the structure of natural kogarkoite $\text{Na}_2\text{SO}_4 \times \text{NaF}$.

This product was not commercially successful as it failed in terms of both chemical composition and properties, especially its whiteness.

Kogarkoite crystals are characterized by a specific shape, i.e. hexagonal prisms and size from 10 to 100 μm (see Figure 2). Kogarkoite has low solubility and is the first to crystallise from evaporated sodium-bicarbonate-sulphate solutions from gas cleaning. Its crystallisation proceeds until fluorine in sodium sulphate solutions is exhausted.

The obtained kogarkoite crystals have a yellowish colour, which explains the low whiteness and yellowish colour of the precipitate. Table 1 presents the chemical analysis of the obtained kogarkoite precipitate carried out using a scanning electron microscope. It can be seen that kogarkoite with higher fluorine content is formed. Probably, the deviation in terms of fluorine

(from the stoichiometric value) may be due to some inaccuracy of the express analysis performed by raster scanning.

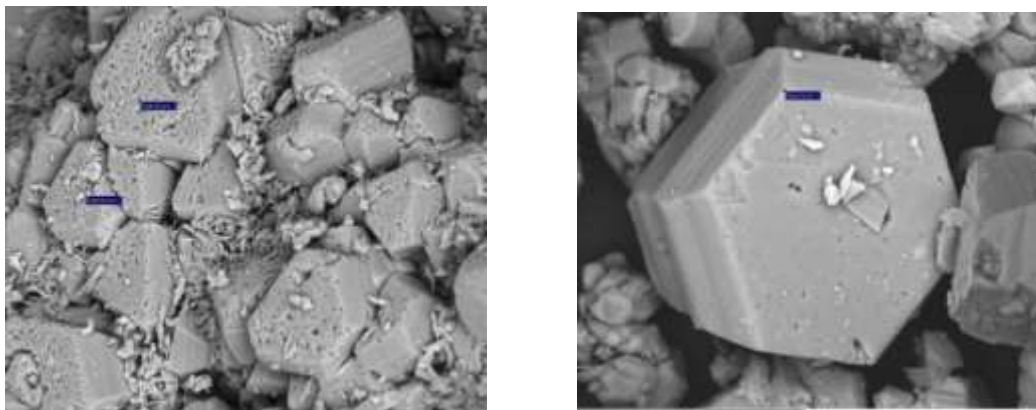


Figure 2. Electronic photograph of the kogarkoite precipitate obtained by evaporation of the scrubbing spent solutions.

Table 1. Chemical composition of kogarkoite samples obtained by evaporation of scrubbing spent solutions.

Sample	Content, wt. %				
	F	Na	S	O	Σ
1	13.03	34.25	16.34	36.38	100.00
2	13.56	33.73	16.41	36.30	100.00
3	16.55	36.46	13.74	33.25	100.00

In selective evaporation, fluoride can be removed from GTC solutions by kogarkoite separation at the first stage, but the kogarkoite mud is not marketable.

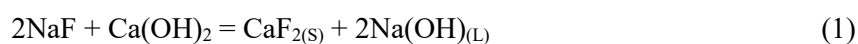
In order to solve the problem of purification of GTC solutions from fluorine, two options of fluoride removal of the gas cleaning spent solution were studied:

- Treatment with lime (CaO) to obtain several products: fluorite mud as a flux additive for Portland cement; sodium sulphate as a marketable product; caustic solution to be used instead of purchased soda for preparation of gas cleaning solutions, including the conversion of sodium bicarbonate into soda;
- Regeneration of secondary cryolite from spent solutions of gas scrubbing.

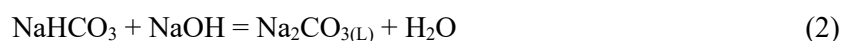
1.1 Treatment with Lime Followed by Evaporation

Treatment of the GTC solution with lime solves several problems:

- To convert ~ 90 % of fluorine into a solid phase in form of fluorite and thus obtain caustic alkali:



- Convert 100 % of sodium bicarbonate into sodium carbonate:



- Convert a substantial portion of sodium carbonate (soda) into caustic:



Lime treatment produces the mud containing 80–85 % of calcite and 15–20 % of fluorite. Tests conducted at the cement plant have shown that this mud can be used as a flux additive at RUSAL's cement plants (RUSAL group of companies is one of the largest producers of Portland cement in Europe). Introduction of ~ 0.5–1 % of this mud allows reducing the sintering temperature of Portland cement clinker by ~ 50 °C.

Treatment of the GTC wet scrubber solution with lime simplifies the salt system (removal of sodium fluoride, conversion of sodium bicarbonate into sodium carbonate, soda causticisation), as well as reducing the solubility of sodium sulphate in a caustic solution by a factor of 2 or more. Evaporation of the resulting solution yields a precipitate consisting of ~ 60 % anhydrous sodium sulphate in form of meta-thenardite and ~ 40 % burkeite $\text{Na}_2\text{CO}_3 \times 2\text{Na}_2\text{SO}_4$. The tests showed that the resulting mixture complies with the requirements of pulp and detergent manufacturers in terms of its performance.

The caustic solution obtained after evaporation and separation of sodium sulphate can be used instead of purchased soda for preparation of GTC wet scrubbing solutions. Due to reaction (2) the sodium bicarbonate is recycled back to the process, which significantly reduces the expenses for purchasing soda ash for wet gas scrubbing.

At KrAZ's pilot facility several pilot tests were carried out to produce several large batches of sodium sulphate (see Figure 3).



Figure 3. Big-bags with sodium sulphate product in the warehouse.

The financial and economic model of the developed technology showed that it has low returns in the investment due to the high cost of purchased lime. Therefore, a more economically viable option was investigated.

1.2 Regeneration of Secondary Cryolite from Gas Cleaning Spent Solutions Followed by Evaporation

To reduce fluorine in the produced sodium sulphate, RUSAL Engineering and Technology Centre developed a technology for regeneration of secondary cryolite from gas cleaning spent solutions that enables to reduce the residual fluorine content to less than 2 g/dm³.

Absence of fluorine in the solution during the evaporation enables the production of a double salt with a structure of natural mineral burkeite $\text{Na}_2\text{CO}_3 \times 2\text{Na}_2\text{SO}_4$. This salt is conventionally referred to as soda-sulphate mixture (hereinafter referred to as SSM). The obtained mixture is practically monomineral, but due to a poor purification of the solution, it still contains chromophores that worsen whiteness and increases the yellowness.

2. Process Development for Cleaning Soda-Sulphate Mixture to Reduce Yellowness and Improve Whiteness to $\geq 80\%$

Removal of suspended solids from the solution. To remove coloured impurities from the defluorinated solution of gas scrubbing, a process of precipitating the suspended solids was devised. An emulsion of synthetic flocculant based on polyacrylates was selected from industrial flocculants used in alumina production. Addition of this flocculant in the amount $\leq 0.8 \text{ g/m}^3$ effectively clarifies the solution by precipitating $\geq 90\%$ of all impurities.

X-ray diffraction analysis of the thickened precipitate showed that said precipitate consists of a mixture of iron scale, fine carbon, cryolite, chiolite, elpasolite $\text{K}_2\text{Na}(\text{AlF}_6)$, dawsonite $\text{NaAlCO}_3(\text{OH})_2$, alumina, and others.

Evaporation of the solution purified from suspended solids and separation of wet soda-sulphate mixture. A rotary flash vessel was used to set the conditions of evaporation and crystallisation of a coarse crystalline soda-sulphate mixture (see Figure 4). It was demonstrated that the primary clarified solution could be evaporated to obtain Na_2SO_4 concentration of no less than $270\text{--}280 \text{ g/dm}^3$. In this case, the yield of the soda-sulphate mixture can amount to approx. 65% or $\sim 85 \text{ kg/m}^3$ of the solution, with large sized burkeite crystals and that filter well on a drum vacuum filter.



Figure 4. Rotary flash vessel RV 10 (IKA).



Figure 5. Portable spectrophotometer CM-600d (Japan) for determination of whiteness and yellowness of soda-sulphate mixture.

To obtain a well-filtered coarse crystalline precipitate of soda-sulphate mixture the following conditions are recommended:

- Cooling the evaporated solution from $+ 71 \text{ }^\circ\text{C}$ to $+ 65 \pm 1.5 \text{ }^\circ\text{C}$; and
- Holding the slurry in the agitated crystallisation vessel for ≥ 30 minutes.

The whiteness index (WI) obtained during evaporation and crystallization of soda-sulphate mixture was measured using CM-600d portable spectrophotometer (see Figure 5).

Grinding of soda-sulphate mixture product to minus 200- μm fraction. To produce a product with whiteness index of above 80 %, the soda-sulphate mixture was grinded to obtain a 95 % minus 200- μm fraction. This solution is of such a quality that we are able extract sustainable products with a whiteness index higher than 85 % that meet the requirements from the end-users.

Industrial implementation, products, replication of the technology. Based on the developed process, a set of design and engineering documentation was developed followed by the construction of a facility that was commissioned for in 2023. (see Figure 6).



Figure 6. Soda-sulphate mixture production facility at Krasnoyarsk aluminium smelter.

Soda-sulphate mixture with high whiteness index produced at the facility is highly appreciated by consumers and the mixture is already used to produce some cleaning agents (see Figure 7).



Figure 7. Goods produced from white soda-sulphate mixture at Krasnoyarsk aluminium smelter.

The developed "Method of soda-sulphate mixture production from recycled soda-sulphate solutions of gas scrubbing of aluminium reduction" is protected by a patent (No. 2819968) granted by the patent office of the Russian Federation.

3. Conclusions

An innovative technology for the utilisation of sodium sulphate from the solutions of the 2nd stage wet gas scrubbing to produce commercial cleaning products was developed and implemented at Krasnoyarsk aluminium smelter. Implementation of said technology enables to eliminate the accumulation of sodium sulphate waste in the tailing retention dykes of RUSAL's aluminium smelters.

The produced soda-sulphate mixture with a high whiteness index complies with the requirements of consumers and is demanded by large consumers in Western Siberia, including detergent manufacturers and pulp and paper industry enterprises.

4. Acknowledgements

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