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 ≥ 95 % burkeite $Na_2CO_3 \times 2Na_2SO_4$ 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

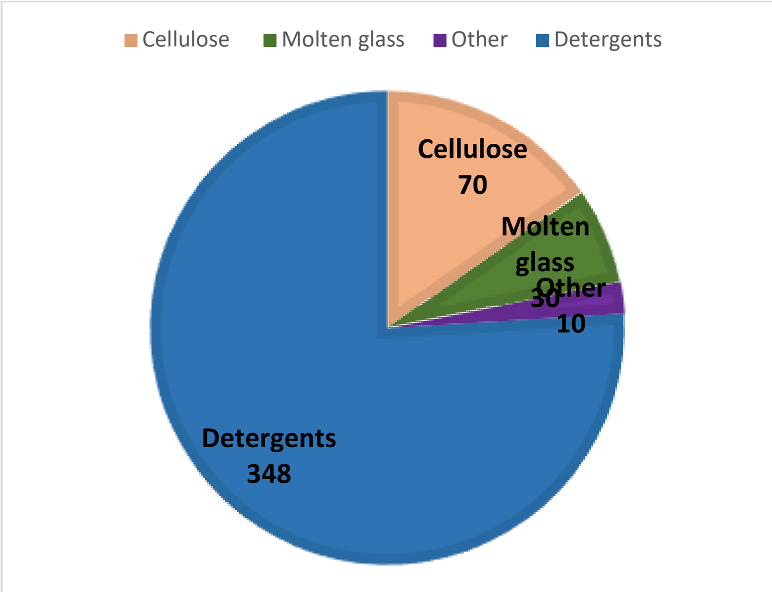

Figure 1. Sodium sulphate consumption, thousand t/a.

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 $Na_2SO_4 \times NaF$.

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