

Thermal and plasma-chemical processing of sulphate wastes

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Abstract

Two-step method of waste $\text{NH}_4 \text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ (alum) valorisation into fine A_2O_3 and elemental sulphur is proposed:

1. Alum calcination in reducing atmosphere at $\sim 600^\circ\text{C}$
2. Hot exit gas processing in a GlidArc reactor

Before 1996 uranium mining was running near Stráž pod Ralskem (Czech Republic) *via* an underground leaching by sulphuric acid (spent >4 millions tons) and other chemicals. Residual underground contamination makes now risk to the mayor drinking water resources.

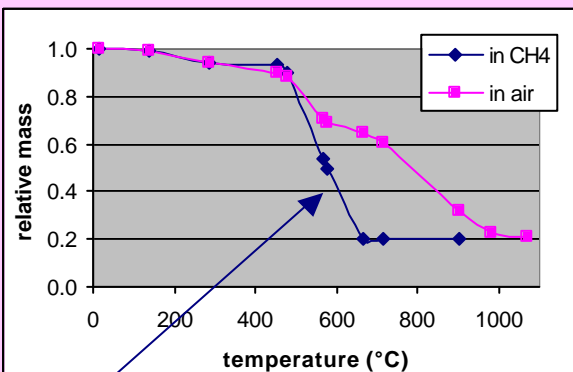
By cleaning this contamination one gets annually 7200 tons of alum and even more tons of other wastes. The entire remediation costs will be €1.6 billion for some 2.8 million tons SO_4^{2-} withdrawn from the ground...

The alum is considered as waste. To avoid a secondary salination of the ground water it should be converted to some less water-soluble solids for a safe disposal. We propose an alternative and valorising process:

Alum + natural gas ? **pure Sulphur** + H_2O + CO_2 + **pure A_2O_3**

Calcination

Gravimetric trials of up to 0.8 kg samples of real Diamo's alum up to 1070°C . All volatile products crossed two temperature-controlled condensers. All gas was analysed using a classical GC.



Evidence: calcinate under reducing atmosphere!

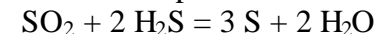
- Our process does not produce SO_3
- Total calcination of the alum is accomplished at $\sim 650^\circ\text{C}$ (400°C less than the open air calcination)
- Presence of N_2 indicates that NH_4^+ and $\text{SO}_3^{2-}/\text{SO}_4^{2-}$ red-ox reactions took place

Calcination of alum should be therefore performed under reducing atmosphere in order to avoid SO_3 , excessive temperatures and heavy corrosion of an oven. Any reductant like natural gas, heavier hydrocarbons, coal, ... can be used. An excess of reductant should not be a problem because we would need it anyway for the final plasma-assisted reduction of SO_2 into elemental sulphur.

Reduction of SO_2

Plasma-catalysed reductive conversion of SO_2 into elemental sulphur was already proposed [1]. Such conversions using light hydrocarbons, CO or a pulverised coal are exothermic ($\sim 100 \text{ kJ}$ per mol of SO_2) and should be spontaneous – but in reality they are kinetically blocked.

The optimal process conditions are near 650°C but a lot of unreacted SO_2 and over-reduced H_2S occur. However, observed $\text{H}_2\text{S}/\text{SO}_2$ ratio is close to 2 that opens a way to the well-known Claus' process of their mutual destruction:



that can be operated after product cooling.

A very active and cold GlidArc catalytic discharge [2] provides all conditions to realise such exothermic reduction:



1. A. Czernichowski, H. Lesueur, J. Polaczek, T. Czech, G. Collin, Cold Plasma Reduction of Sulfur Dioxide to Elemental Sulfur, *Erdöl, Kohle, Erdgas, Petrochemie*, vol. 48(1), 30-32 (1995)
2. A. Czernichowski, P. Czernichowski, GlidArc-assisted cleaning of flue gas from destruction of conventional or chemical weapons, *this Conference*

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www.glidarc-tech.com