

Thermal and plasma-chemical processing of sulphate wastes

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Abstract

Alternative method of waste ammonium/aluminium sulphate $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum) valorisation into fine Al_2O_3 and elemental sulphur is proposed in two steps: a calcination in reducing atmosphere of natural gas at the relatively low temperatures around 600°C followed immediately by the hot exit gas processing in a GlidArc plasma reactor. Water, CO_2 and solid elementary sulphur are recovered as final products after the second step.

Keywords: ammonium-aluminium alum, sulphur dioxide, sulphur, GlidArc

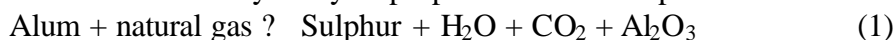
1. Introduction

Between 1967 and 1996 uranium mining was running near Stráž pod Ralskem (Czech Republic) *via* an underground "in situ" leaching by a water solution of sulphuric acid. In order to extract 15 thousand tons of uranium some 400 millions of m^3 of leaching fluid were used (more than 4 millions tons of sulphuric acid, 313 thousand tons of nitric acid, 112 thousands of ammonia, and 26 thousands tons of hydrofluoric acid).

Nowadays, the residual underground contamination from the leaching process makes risk to the mayor drinking water resource located very close to the mining site. To prevent leaking of contaminated leaching water into the drinking water supplies, Diamo (a state enterprise, past and present operator of the site, see www.diamo.cz) is continually pumping the leaching water from up to 400-m depth. In evaporation plant this solution is concentrated, some residual uranium is extracted, and during the following crystallization the ammonium/aluminium sulphate $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ called "alum" is obtained. The cleaning of contaminated water produces annually 80 tons of uranium, 7200 tons of alum and 230 thousand m^3 of sludge. The entire remediation process is expected to finish by 2035 at its total costs is estimated as €1.6 billion. During this period 3.7 million tons of contaminants (2.8 million tons SO_4^{2-}) will be withdrawn from the ground.

The alum is mostly considered as waste. For economical reasons and to avoid a secondary salination of the ground water the alum should be processed in order to get some commercial products and/or less water-soluble solids to be safely disposed. It is therefore converted by calcination into aluminium sulphate used in the paper industry or is added to fertilizers.

This paper describes our feasibility study of proposed alternative process:



in which one would recover a pure fine alumina powder for ceramic industry or for aluminium metal production. As concerns sulphur, we have already shown that a plasma-assisted reduction of concentrated SO_2 to elementary sulphur is possible [1] that would ease the whole process (1).

2. Experimental

2.1. Calcination

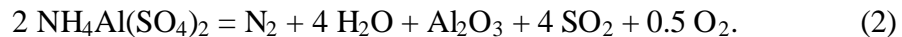
We have first executed several gravimetric trials of calcination of macro-samples (up to 0.8 kg) of real Diamo's alum up to 1070°C using a 1.5 kW electric oven. The oven temperature was rising at about 10 K/min rate. The residual solid was weighted (see Fig. 1) while all volatile products crossed two temperature-controlled condensers.

Figure 1

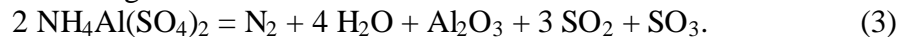
Sublimates were mostly collected in the first hot condenser while liquid condensate was collected in the next cold condenser. All remaining gas emitted from the sample was analysed using a classical gas chromatography. Our initial tests gave the following results:

- Between 20 and ~200°C: drying from residual moisture and then the hydrate decomposition
- Between ~200 and 300°C: SO₂ emission (its concentration reached ~4 vol.% at ~430°C and ~70 vol.% at 800°C)
- Free NH₃ emission at only ~1 vol.% level at up to 560°C
- N₂ presence at whole range of temperatures, from 81 vol.% at 430°C down to 22 vol.% at 800°C
- Very strange curve of O₂ observed: starting from 13 vol.% at 430°C to zero at 560°C and appearing again up to 6 vol.% at 800°C
- The most marked alum calcination between 500 and 700°C
- SO₃ emission at the end of calcination, starting from 700°C.

The calcination of the anhydrous salt gave only minor amount of free ammonia and a bit more of (NH₄)₂SO₄ and/or (NH₄)₂SO₃ and/or similar sublimates (max. 2 % of initial alum mass). Instead, we rather observed some reduction/oxidation processes in which one obtains a quasi-total salt decomposition:



A part of anhydrous salt decomposes also to SO₃ recognised by its characteristic heavy smog exiting the oven at the temperatures higher than 700°C:



This highly corrosive SO₃ decomposed partially at higher temperatures at the end of the calcination:



In order to avoid SO₃ – a calcination under reducing atmosphere appeared as evidence. Such calcination of 376 g initial alum under 0.5 L/min methane flow rate at 1.2 kW oven power is illustrated on Figs. 1 and 2. Table 1 presents the exit gas analysis (by gas chromatography, dry basis) performed at eight temperature events. Perhaps the gas composition is somehow perturbed by a reaction of gases with very hot stainless steel walls around the quartz test-tube? An inspection of the internal walls after the tests showed a large amount of dark dross...

Figure 2

Table 1

We see however that:

- Process does not produce SO₃
- Total calcination of the alum is accomplished at ~650°C (so about 400°C less than the open air calcination)
- Presence of N₂ indicates that NH₄⁺ and SO₃⁻²/SO₄⁻² red-ox reactions still took place
- Very fast process occurs at about 550°C.

As a draft conclusion we state that calcination of alum should be performed under reducing atmosphere in order to avoid SO₃, excessive temperatures and therefore heavy corrosion of an oven. Any reductant like CH₄, natural gas, heavier hydrocarbons (or perhaps even coal), H₂, CO, H₂+CO (syngas) 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 the main pollutant (SO₂) into elemental sulphur.

2.2. Reduction of sulphur dioxide SO₂

As the calcination tests in which fine, commercial-grade Al₂O₃ was separated from remaining volatile compounds was done, we could then deal with the waste SO₂ problem. Plasma-catalysed

reductive conversion of SO_x into elemental sulphur [1] was already proposed. Such conversions using light hydrocarbons, CO or even a pulverised coal are exothermic and should be spontaneous – but in reality they are kinetically blocked according to literature. Figure 3 presents the thermodynamic equilibrium system of $2 \text{SO}_2 + \text{CH}_4$ in 650 – 900 K temperature range and under 1 bar pressure (our calculation based on [2]).

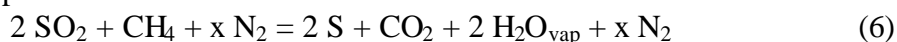
Figure 3

The optimal process (1) conditions are expected near 650°C but a lot of unreacted SO_2 and over-reduced H_2S occur. However, observed $\text{H}_2\text{S}/\text{SO}_2$ molar ratio is close to 2 that opens a way to the well-known Claus' process of their auto-destruction:



that can be operated after product cooling.

A very active GlidArc cold catalytic discharge [3] provides necessary conditions to realise the reduction. Our target process can be written as:



that is an exothermic process in which the standard enthalpy ΔH° is equal to $-104.3 \text{ kJ per mol of SO}_2$.

A 6-electrode 2-L GlidArc-I reactor was used at atmospheric pressure. The first trials were made using pure N_2 , SO_2 , and CH_4 gases (from gas cylinders) dynamically mixed. Mass controllers regulated their flow-rates while the power dissipated in GlidArc (measured on the mains) was below 1 kW. The products exiting the plasma crossed a filter where yellow sulphur dust was collected (other part of sulphur was leaving the reactor under molten form). Carbon black was absent. Dry gas analyses showed us however a presence of H_2 and CO indicating rather a process:



which is endothermic ($\Delta H^\circ = +225.5 \text{ kJ/mol SO}_2$).

More systematic trials were then performed using again methane but also hydrogen or carbon monoxide as reductants. Table 2 presents some Input/Output data related to these tests.

Table 2

From CO/ CO_2 ratios we could roughly estimate that 30 – 50 % of methane reacts according to the process (7) while the remaining CH_4 goes *via* reaction (6). From the mass balance for this bench scale feasibility tests we deduce a quite good conversion rate of SO_2 in the range of 30 to 80% at the energy expense in the range of 3.5 – 10 kWh per kg of recovered solid sulphur. We cannot expect at the same time a very high SO_2 conversion rate and a reasonable energy expense so that some gas recycling *via* a sorption/desorption technique should be applied for total neutralisation/recovery of the sulphur. Such recycling technologies already exist at an industrial scale...

As concerns the energy expense we expect it at much lower level for our new GlidArc generators at industrial scale. Moreover, we expect also some partial sulphur recovery in the calcination step so that the total SO_2 stream to process could be lower. And what happens if higher hydrocarbons (like LPG) or resulting syngas ($\text{H}_2 + \text{CO}$) are used as reductants?

3. Conclusion

Our proposed alternative method of waste ammonium/aluminium sulphate (alum) $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ valorisation into fine Al_2O_3 and elemental sulphur is feasible. Two steps are necessary: a calcination in reducing atmosphere so that it happens at a relatively low temperature around 600°C and a reduction of the hot gas from calcination in a GlidArc plasma reactor. Water, CO_2

and solid elementary sulphur are recovered as final products after the second step while the first calcination step gives a fine and pure Al_2O_3 .

We hope that our findings can be useful to solve similar environmental problems elsewhere and/or to contribute to the SO_2 removal technology related to the coal- or oil-fired plants as well in other industries.

References

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Figures

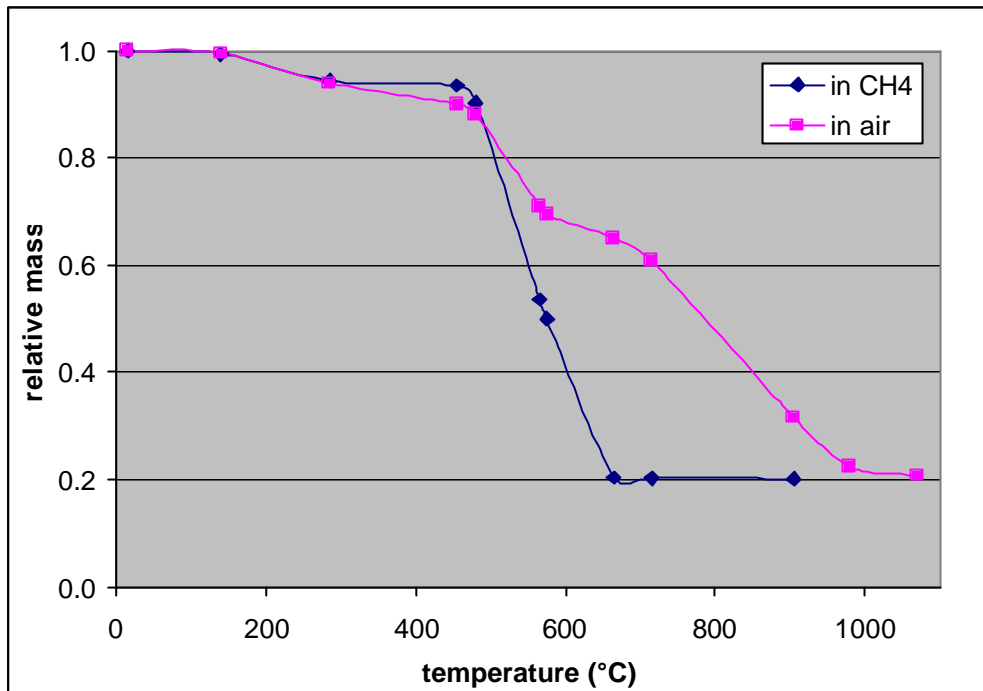


Fig. 1. Thermo-gravimetric behaviour of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (alum) heated in air or in methane at the rate of $10^\circ\text{C}/\text{min}$

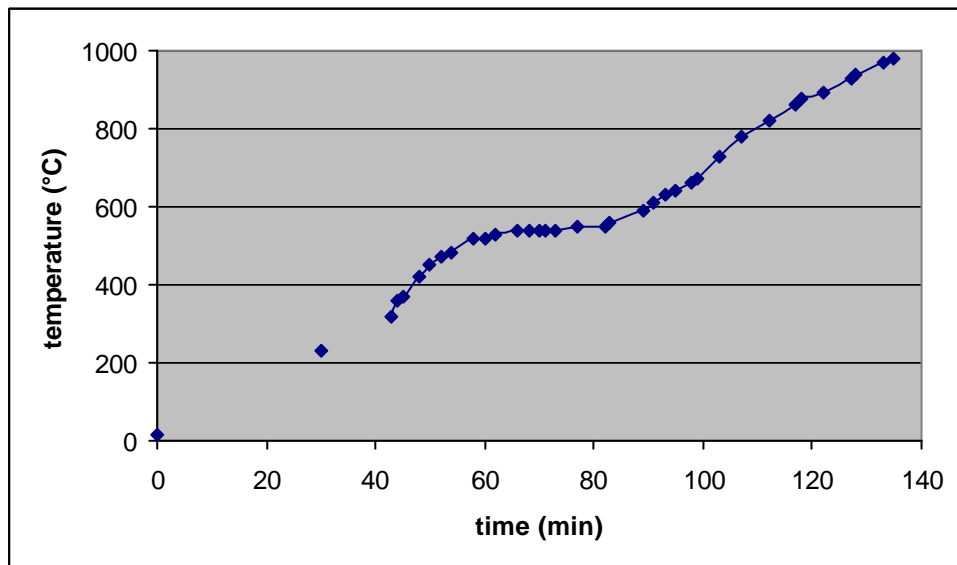


Fig. 2. Time-resolved temperature evolution during alum calcination in a weak flow of methane (related to Fig. 1 conditions)

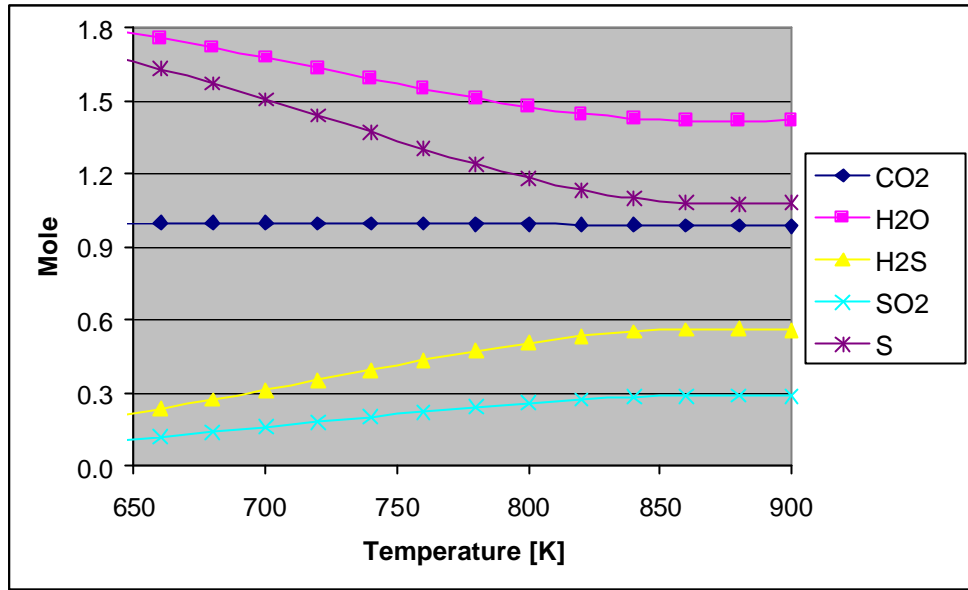


Fig. 3. Thermodynamic equilibrium system of $2 \text{SO}_2 + \text{CH}_4$ under 1 bar pressure

Tables

Table 1. Composition of gas (in vol.%) emitted during calcination of alum under limited flow of methane. This test is related to Figs. 1 and 2 conditions.

Temp. °C	Exit gas concentration (vol.%)					
	CO ₂	N ₂	CH ₄	CO	SO ₂	H ₂
40	0	0	100	0	0	0
180	1.2	0	99	0	0	0
450	5.0	36	55	0.1	0	3.2
540	6.5	34	12	0.3	46	1.4
560	8.2	20	2.3	0.2	66	n.a.
670	13	15	0.4	0.1	66	n.a.
860	18	10	0.3	0.1	67	n.a.
980	28	6.1	0.1	0.1	58	n.a.

Table 2. Some Input/Output data of selected tests of GlidArc-assisted reduction of SO₂ using natural gas (NG), Hydrogen or Carbon monoxide as reductants.

Test		1	2	3	4	5	7	8	9	11
GlidArc Power [kW]		0.45	0.40	0.92	0.90	0.50	0.97	0.97	0.85	0.86
Input flow-rate L(n)/min	N ₂	2.0	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
	SO ₂	3.0	3.5	3.7	2.9	2.8	2.6	2.9	3.1	3.2
	CH ₄	3.7	3.6	3.3	3.6					
	H ₂					4.6	8.3	11		
	CO								11	8.6
	total	8.7	8.5	8.4	7.9	8.7	12	15	16	13
SEI [kWh/m ³ (n)]		0.86	0.79	1.8	1.9	0.95	1.3	1.1	0.88	1.1
Conversion of S [%]		35	38	49	48	34	82	74	65	31
SER [kWh/kg S]		5.0	3.5	5.8	7.5	6.1	5.3	5.3	5.1	9.8
Composition of exit gas (vol.%)	CO ₂	1.1	2.3	4.1	2.1			0.2	12	14
	N ₂	23	19	19	18	28	20	17	8.7	10
	CO	10	11	15	16				63	54
	SO ₂	22	29	24	19	37	6.1	8.8	13	18
	H ₂	15	13	18	21	32	71	72		
	CH ₄	27	22	18	21					
	C ₂₊	0.4	0.3	0.3	0.3					
	H ₂ O _{vap}	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	

Remarks: L(n) means normal (STP) litres; SEI means Standard Energy Input in kWh per 1 m³(n) of input gas mixture; this value corresponds somehow to the plasma energy density (averaged in time and space); Conversion of S means a molar ratio of recovered solid sulphur to the sulphur contained in the initial SO₂ input; SER means Standard Energy Requirement (in kWh) to recover 1 kg of solid sulphur