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# METHOD FOR UTILIZATION OF THE SULFURIC ACID OBTAINED DURING AUTOCLAVE DISSOLUTION OF PYRITE CONCENTRATE

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## Abstract

*At the high-temperature and oxidation dissolution of pyrite concentrate in the autoclave were produced solutions with a high concentration of ferric ions and a free sulfuric acid (>60 $gL^{-1}$).*

*In our previous studies, the possibility of crystallization of Ammonium Ferric Dodecahydrate and Ferric Sulfate Hydrate from these solutions was proved.*

*The problem of sulfuric acid recovery still remains unresolved. Complete neutralization of $H_2SO_4$ results in gypsum heavily contaminated with iron and other non-ferrous metals. It is a waste product and is deposited in tailings ponds or mountainous terrain, which leads to environmental pollution. A partial neutralization (up to 70%) of sulfuric acids with a high concentration of $Fe^{3+}$ ion solutions has been proposed. The resulting gypsum was with high purity (0.05% Fe).*

*The objective of this study is determine of optimal technological parameters of the conversion process of the gypsum waste obtained during a partial neutralization to ammonium sulfate, a commercial product that can be used in agriculture as artificial fertilizer.*

*Based on experimental results the counter-current scheme of the conversion process is proposed.*

- ***Keywords:*** *acidic ferric-sulfate solutions, neutralization, gypsum waste, conversion process*

## Materials and research methodology

**Table 1** - Chemical composition of the solution, g/L

| $Fe^{3+}$ | $Fe^{2+}$ | Na | K | Mg | Mn | Mo | Ni | Pb |
|---|---|---|---|---|---|---|---|---|
| 58,54 | 1,40 | 0,1 | 0,1 | <0,01 | 0,016 | 0,025 | 0,076 | 0,040 |
| **Co** | **Sb** | **Sn** | **P** | **Al** | **Bi** | **Ca** | **As** | **$H_2SO_4$** |
| 0,008 | <0,01 | 0,064 | <0,01 | 0,9 | 0,018 | 0,20 | 0,11 | 61,5 |

**Table 2** - Chemical silicate analysis of marble-cutting waste, fine fraction (MFF), % w/w

| CaO ($CaCO_3$) | MgO ($MgCO_3$) | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | Others |
|---|---|---|---|---|---|---|
| 52,75 (94,15) | 1,70 (3,55) | 0,81 | 1,08 | 0,06 | 0,01 | 0,34 |

**Table 3** - Size distribution in marble-cutting waste, fine fraction (MFF)

| Size of fraction | <10 µm | -20+10 µm | -30+20 µm | -40+30 µm | -50+40 µm | -70+50 µm | -100+70 µm |
|---|---|---|---|---|---|---|---|
| Share in % | 49,6 | 37,6 | 11,0 | 1,6 | 0,2 | 0,0 | 0,0 |

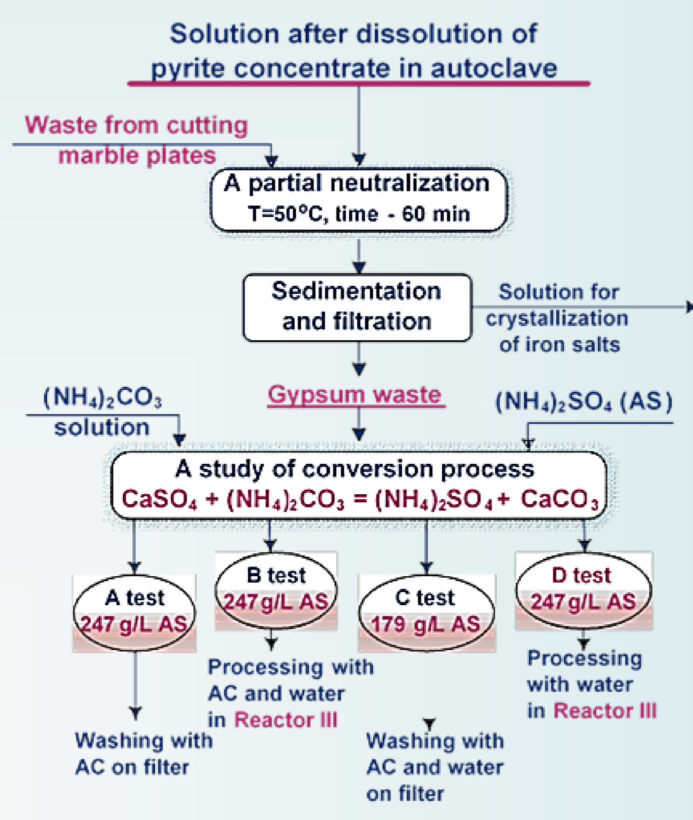


**Figure 1** - Schematic diagram for conducting of the experiments

The methodology involves two main processes:

- a partial neutralization of free sulfuric acid with MFF - reaction (1)
- conversion of the resulting gypsum to ammonium sulfate by the Merseberg reaction (2):

$$H_2SO_4 + CaCO_3 + H_2O = CaSO_4.2H_2O \quad (1)$$

$$CaSO_4.2H_2O + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4 + 2H_2O \quad (2)$$

The degree of conversion ($\alpha$) was calculated by the following formula:

$$\alpha = \left\{ \frac{[(M_{gypsum}.S_{SO4,gypsum}) - (M_{sludge}.\%S_{SO4,sludge}}{M_{gypsum}.\%S_{SO4,gypsum}} \right\}.100, \%$$

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## Experimental Results

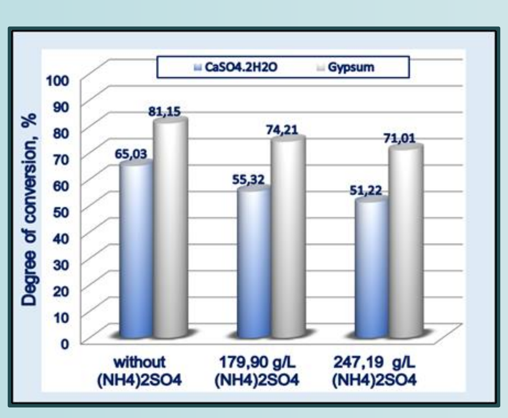


**Figure 2** – Effect of $(NH_4)_2SO_4$ concentration in the solution on the degree of conversion of gypsum waste and chemical reagent. (RI)

**Table 4** - Chemical composition of the filtrate and sludge

| | Parameter | Test A | Test B | Test C | Test D |
|---|---|---|---|---|---|
| RI | $(NH_4)_2SO_4$, $g.L^{-1}$ | 247* 341,56 | 247* 314,43 | 179* 271,13 | 247* 367,85 |
| | $(NH_4)_2CO_3$, $g.L^{-1}$ | 6,72 | 6,72 | 4,80 | 6,72 |
| RII | $(NH_4)_2SO_4$, $g.L^{-1}$ | 148,94 | 157,77 | 76,65 | 78,99 |
| | $(NH_4)_2CO_3$, $g.L^{-1}$ | 72,0 | 172,0 | 249,76 | 239,12 |
| | Washing of the sludge from RII with 33% $(NH_4)_2CO_3$ solution on the filter | yes | - | - | - |
| RIII | Processing of the sludge with 33% solution of AC and water in Reactor III | - | yes | - | - |
| | Washing of the sludge with 33% solution of AC and water on filter | - | - | yes | - |
| | Processing of the sludge with water in Reactor III | - | - | - | yes |
| Content of $S_{SO4}$, in carbonate sludge, % | | 6,16 | 0,55 | 2,58 | 1,24 |
| Degree of conversion, % | | 93,91 | 99,0 | 97,24 | 97,78 |

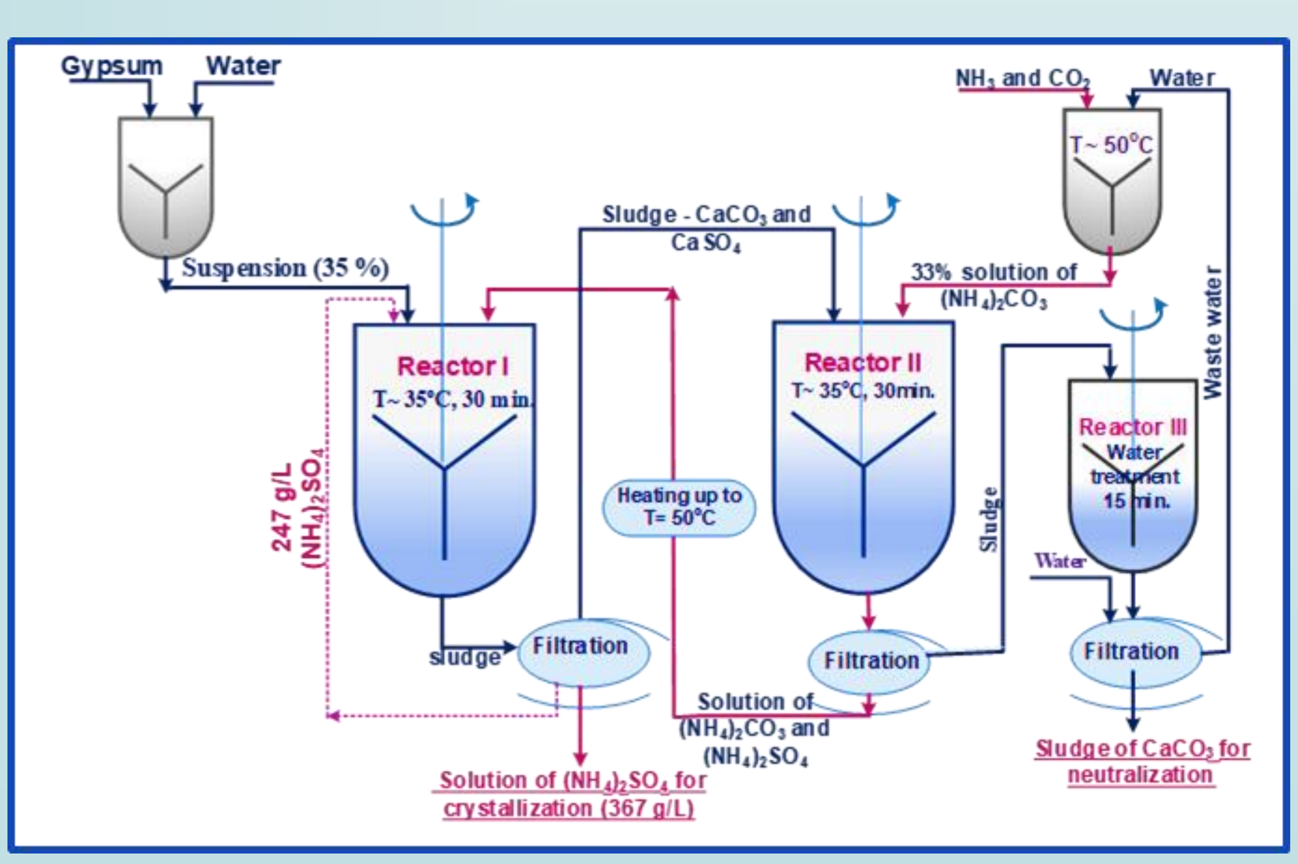


**Figure 3** - Principal counter-current scheme of conversion process of gypsum waste to concentrated ammonium sulfate solution

## Conclusions

Optimal parameters of the conversion process have been determined: 50% excess of $(NH_4)_2CO_3$, T=35 °C; reaction time 30 min. The conversion in I reactor was conducted in the present of $(NH_4)_2SO_4$ (247 g/l). The obtained in reactor II precipitate was treated with water in reactor III.

The products of the conversion process were: concentrated ammonium sulfate solution (367 g/L) and $CaCO_3$ precipitate.

The solution is being sent for a crystallization of $(NH_4)_2SO_4$ – an artificial fertilizer, which can be used in agriculture. The obtained precipitate of $CaCO_3$ contains 1,24% sulfate sulfur ($S_{SO4}$) and it comes back for the neutralization of the initial ferric sulfate solutions. The achieved maximum degree of a conversion of a gypsum to ammonium sulfate is 97,78 %. Based on the experimental results, the counter-current scheme of the conversion process is proposed.

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