DOI: http://doi.org/10.21698/simi.2017.0008

MINE WATER TREATMENT TESTS RESULTS FOR A CONTINUOUS FLOW REACTION SYSTEM

Laurentiu Razvan Dinu[1], Valeriu Badescu[1], Violeta Dediu[1], Ionut Cristea[1], Viorel Patroescu[1], Voicu Oncu[2]

[1]National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podu Dambovitei, 060652, Bucharest, Romania, *tehnologi@incdecoind.ro*
[2]SC CEPROMIN SA, 37A 22 Decembrie, Deva, Romania, *office@cepromin.ro*

Abstract

An experimental study has been carried out to assess sulphate precipitation via ettringite process from acid mine water (AMD) originating from closed non-ferrous Romanian mining areas. Such a treatment is required, because by conventional treatment of the AMD with calcium hydroxide, the conformity for sulphate will not be achieved, because the concentration correlated to gypsum solubility exceeds the limit value by roughly three times. Although sulphate is considered benign or with low toxicity, some countries have set limits for the wastewater discharged to natural receivers, from 500 to 1000 mg/L or 600 mg/L in Romania.

The process of sulphate precipitation as ettringite using solid aluminium sources is known to be slow. Tests for sulphate precipitation, using monocalcium aluminate cement as source of reactive aluminium for the ettringite formation were done using continuous flow mixed flow reactors in series (or continuous stirred reactors, CSTR). This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration which can be used further for various design tasks. The reaction rate for sulphate concentration below 600 mg/L may be less than 5 mg/L/min, depending on working conditions. The mixed flow reactors series has a net advantage over single CSTR, the best choice for a full scale treatment plant is a mixed flow reactors series also, as the results indicate that a system with a single mixed flow reactor is to be much larger.

Keywords: *CSTR, ettringite, mine water, sulphate*

Introduction

By treating the mine water with calcium hydroxide (the most common technological approach), the pH is adjusted to 8.5 ÷ 10.5 and the heavy metal ions will precipitate as oxo and hydroxy compounds, together with some gypsum if the initial sulphate concentration is higher than 1500 mg/L. This kind of treatment cannot remove sulphate beyond the concentration corresponding to gypsum solubility (Aube 2015*)*, besides the solution will remain supersaturated with calcium sulphate and improvements can be done by seeded gypsum crystallization and further by advanced sulphate removal, *e.g.* by membrane separation (Chesters et al. 2016) or ettringite precipitation (Ramsay et al. 2001; Kastle et al. 1990).

Sulphate concentration c(SO_4^{2-}) in mine water is typically high and the usage of water downstream can be affected (Meays 2013) that's so, despite the fact that sulphate is not an acute toxic compound, limits for discharge are stipulated, depending on country and sometimes depending on region, typically 250 to 1000 mg/L. As discussed above, these limits, lower than 1500 mg/L, cannot be met using conventional treatment methods. Sulphate precipitation as ettringite, calcium sulphoaluminate, $3CaO•3CaSO_4•Al_2O_3•32H_2O$) is an effective AMD treatment alternative and it is using aluminium containing reagents (Janneck et al. 2013).

An experimental study has been carried out to assess sulphate precipitation via ettringite process from AMDs originating from closed non-ferrous mining sites in the North Romanian mining area. Because the study was conducted at pilot level with continuous flow, multistage reaction system, it was able to provide useful data for the sulphate apparent precipitation kinetic. Evaluation of the overall kinetics of the reaction from flow-through tests is used by others also (Dietz et al. 2002).

Experimental

Mine water was treated in a three stage continuous flow process: metal oxidation and precipitation, ettringite precipitation and final pH adjustment, according to the flow sheet shown in Fig. 1. The performance requirements were in accordance with Romanian NTPA001, including the limit of 600 mg/L for sulphate ion, SO_4^{2-}.

Each of the reaction sub-systems for the first two stages comprised of a cascade continuous flow stirred reactors followed by vertical type settlers. The detailed design of the pilot plant was done by WISUTEC Umwelttechnik GmbH. Each reactor was equipped with mechanical mixer, direct drive, 3 blades propeller, Da = 0.225 m, n = 725 rpm and with individual pH control assembly (PID) with dosing pump for lime milk.

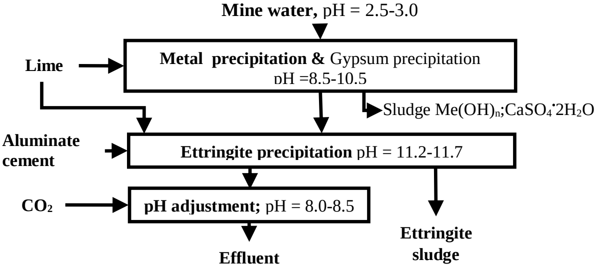

Figure 1. Pilot level basic flow-sheet for the AMD treatment

Ettringite precipitation module had three reactors R1 to R3 and a settler, according to Fig. 2. A fourth agitated vessel R4 in series (not shown in Fig. 2) acts as a feed tank for a daw-off pump which works by level control for R4, kept to a about 50% of total height. The estimated mixing parameters and the space-time values (corresponding to the working flow rate of 0.5 m^3/h or 1.0 m^3/h, as used, are shown in Table 1. Solid calcium aluminate cement (CA) was fed to the first reactor by a screw feeder with variable speed, adjusted manually to the required solids dosing rate. Lime milk was pumped to each reactor to keep the pH value between 11.2 to 11.4. *Calucem* monocalcium aluminate cement with Al content of 50% as Al_2O_3 was used (fineness, Blaine 3300-3800 cm^2/g, residue on sieve at 90 μm < 3%).

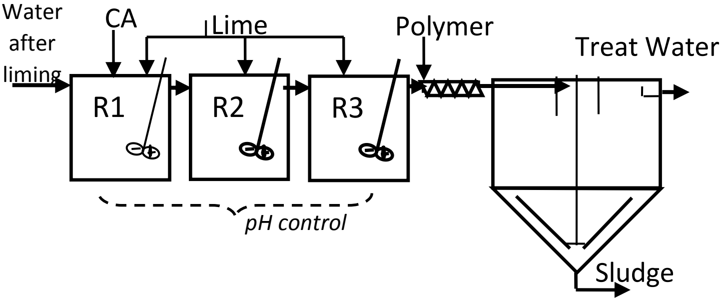

Figure 2. Basic flow-sheet of the ettringite precipitation sub-system
"CA" - calcium aluminate cement

Table 1. Ettringite reactors parameters

Parameter	Units	R1	R2	R3	R4	System
Space-time ($Q = 0.5\ m^3/h$)	h	1.0	0.8	0.8	*	2.6
($Q = 1.0\ m^3/h$)	h	0.5	0.4	0.4	0.2	1.5
Velocity gradient, G	s^{-1}	485	545	545	775	-
Dissipated power, P/V	W/m^3	710	885	885	1800	-

*Without sampling

For any change of parameters, the system was allowed to work for at least 10 times of total system space-time to reach the new steady-state and samples were drawn from ettringite reactors to assess the sulphate concentration. This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration which can be used further for various design tasks.

The treatment process was studied for several mine water sources originating in some Romanian mining perimeters, of which two are representing the *Case studies **1*** and ***2***, selective results being presented here. Each case study was structured with several *Runs*, having specific process parameters sets.

Results and Discussion

Modelling the pilot plant ettringite reaction system as ideal CSTRs in series (or mixed flow reactors), so each reactor steady-state is characterized by uniform concentration and also by constant in time concentration, there is a stepwise change in concentration from reactor to reactor. For any set of operating conditions, samples taken from each reactor allow to quantify the conversion for each space-time value, if sampling is done in steady-state. Thereby the assessment of the time required for the system to reach the steady state is important. For the ideal CSTR that has experienced a step decrease in feed concentration, the exit concentration dependence is (Davis et al. 2003):

$$C / C_0 = e^{(-t/\tau)} \qquad (1)$$

where $C_{A,0}$ is the inflow initial tracer concentration and C is the reactor concentration, $\tau = V/Q$ is the space-time, V is the reactor volume, Q is the volumetric flow rate and t is the time after the step change had occurred.

Computing for the R1 to R3 series the ratio C/C_0 as a function of the reduced time

$\theta = t / \tau_s$, where τ_s is the total system space-time, we have found that a value of $\theta > 3$ is required for the step perturbation to level out including for R3 (see Fig. 3). For our pilot level tests a minimum run time of 15 or 24 h (at least eightfold of total reaction system residence time) was considered enough to reach steady state.

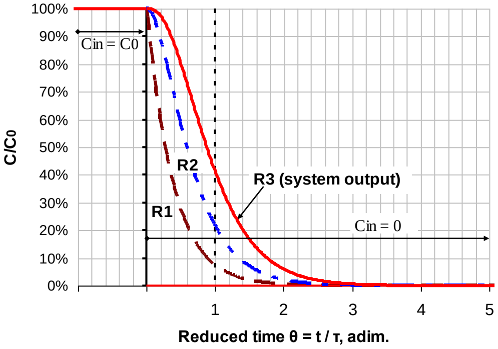

Figure 3. Stabilization of the CSTR series output calculated for a step perturbation (inlet concentration step decrease from $C_{in} = C_0 \neq 0$ to $C_{in} = 0$)

The sulphate concentration after metal precipitation settler (inflow for the ettringite precipitation stage) was 2800 mg/L to 2650 mg/L for the *Case Study **1*** mine water and 1940 mg/L to 1725 mg/L for the *Case study **2*** mine water.

The sulphate concentration profiles (sulphate concentration dependence of the space-time, along the reaction chain) in the ettringite precipitation reactors, for the two case studies and several runs are shown in Figures 4 and 5, respectively. Results for the *Case study **1*** for two runs are presented here, with different CA doses, 0.82 kg/kg SO_4^{2-} (*Run 1*) and 0.98 kg/ kg SO_4^{2-} (*Run 2*), the two runs being different from each other by some proprietary operational approaches also. Results for the for the *Case study **2***, for three runs with a CA dose of 0.95 kg /kg SO_4^{2-}, of which the 3rd *Run* was operated with a flow rate of 1 m³/h with sampling for R1 to R4. The target sulphate concentration, 600 mg/L, can be effectively and safely reached only for a total system time of 2.6 h for the two case studies.

The reaction rate values can be calculated for each reactor considering the mass balance equation for an ideal stirred tank reactor CSTR operating at steady state which for the case of constant density is (Levenspiel 1999):

$$(C_{A,0} - C_A) = - \tau \bullet r_A (C_{A,f,}) \qquad (2)$$

where $C_{A,0}$ is the inflow concentration and $C_{A,f}$ is the reactor concentration for the component *A* (SO_4^{2-}, this case), $\tau = V/Q$ is the space-time and $r_A(C_{A,f})$ is the reaction rate, which is a function of $C_{A,f}$. For our particular reaction system, the reaction rate for sulphate was calculated for each reactor that is to say for each reactor sulphate concentration (Fig. 5 and 6).

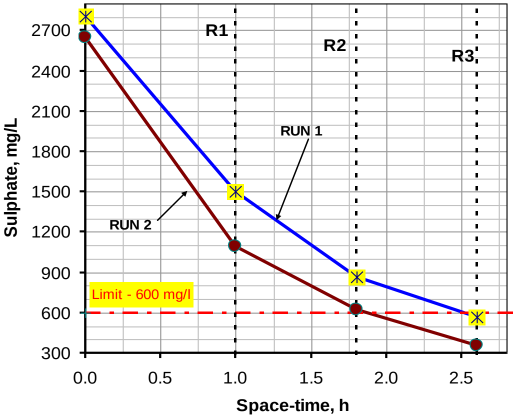

Figure 4. Sulphate concentration profile for the CSTR series - Case study 1

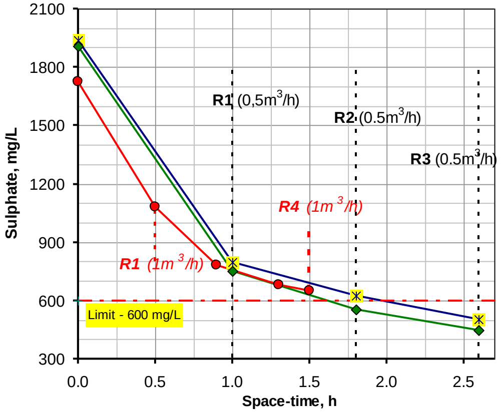

Figure 5. Sulphate concentration profile for the CSTR series - Case study 2

As the reaction rate is a result of a set of parameters, but also technicalities which are not detailed here, the values shown here are informative and of greater importance being the further discussion about the reaction system. With the assumption that the conversion for sulphate is to be obtained with the same performances as for the CSTR series, but using only one CSTR, the aluminate concentration for this reactor and also the sulphate reaction rate can be fairly approximated by those for the last reactor in the series Rx (x = 2 to 4), when the Rx effluent sulphate concentration is considered low enough. It can be computed that for the single reactor case, the space-time required, $\boldsymbol{\tau}_{\mathbf{1\ CSTR}}$, will be around 2 to 5 times higher than for the CSTR series and the same working parameters (Table 2 and 3).

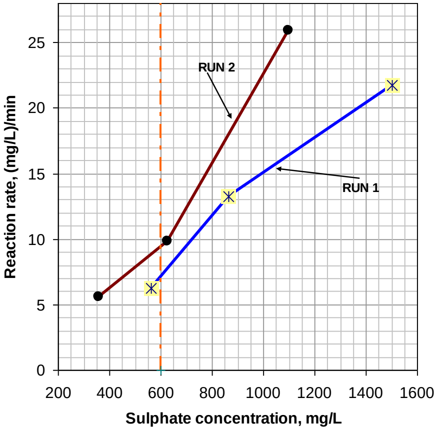

Figure 6. Sulphate precipitation rate - *Case study 1*

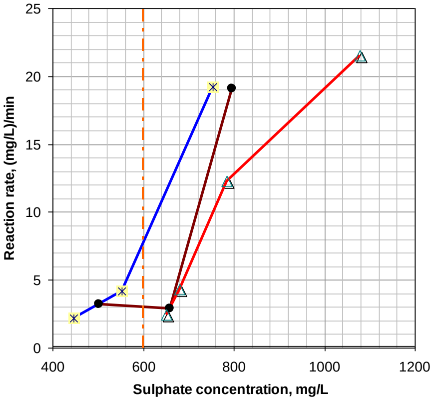

Figure 7. Sulphate precipitation rate - *Case study 2*

Important differences regarding sulphate precipitation yield and required reaction time between batch and continuous flow reaction system can be stressed on. Laboratory batch test results, showed that sulphate concentration values below 600 mg/L can be achieved for batch reaction time below 1.5 h for the both case studies, using reaction conditions close to that for the pilot plant, CA dose, temperature, etc. Despite the fact that, for some conditions, the reaction time requirements for the batch and continuous flow may look similar, this happens only for the CSTR series and it is obvious that the batch reaction time should not be used to assess the requirements for the continuous flow systems. If a proper kinetic law cannot be obtained from batch tests, the batch reaction time needed to obtain a certain conversion is only indicative.

Table 2. Space time required for a single reactor vs. CSTR series (Case study 1)

RUN -	**C_0** mg/L	**C_f** mg/L	**$\Delta c(SO_4^{2-})$** mg/L	**$r(C_f)$** mg/L/min	**$\tau_{1\ CSTR}$** h	**$\Sigma(\tau_{series})$** h
Comparison with the series R1 to R3						
1	2803	564	2239	6.3	5.9	2.6
2	2650	357	2293	5.6	6.9	2.6
Comparison with the series R1 to R2						
1	2803	864	1939	13.3	2.5	1.8
2	2650	625	2025	9.8	3.5	1.8

$\Sigma(\tau_{series})$ - Total space-time for CSTR series (experimental)
$\tau_{1\ CSTR}$ - The space-time required for a single CSTR (computed)
Temperature: 15.5 ± 0.7 ºC

Table 3. Space time required for a single reactor vs. CSTR series (Case study 2)

RUN -	**C_0** mg/L	**C_f** mg/L	**$\Delta c(SO_4^{2-})$** mg/L	**$r(C_f)$** mg/L/min	**$\tau_{1\ CSTR}$** h	**$\Sigma(\tau_{series})$** h
Comparison with the series R1 to R3 (run 1&2) or R1 to R4 (run 3)						
1	1906	446	1460	2.21	11.0	2.6
2	1940	503	1437	2.54	9.4	2.6
3	1725	651	1074	2.42	7.4	1.5
Comparison with the series R1 to R2 (run 1&2) or R1 to R3 (run 3)						
1	1906	552	1354	4.19	5.4	1.8
2	1940	625	1315	3.56	6.2	1.8
3	1725	680	1045	4.33	4.0	1.3

Temperature: 14.0± 0.6 ºC

Conclusions

Using for the continuous flow tests a series of mixed flow reactors gave important, useful results for the kinetic of the ettringite precipitation using solid aluminium source. This reaction system allows the direct determination of the apparent reaction rate versus sulphate concentration, which can be used further for various design tasks. When using calcium aluminate cement as the aluminium source, the reaction rate for sulphate concentration below 600 mg/L may be quite low, e.g 2.5 mg/L/min (no more than 6.3 mg/L/min) and represents the parameter to be used for basic design phase. The best choice for a full scale treatment plant is a mixed flow reactors series also, as the results indicate that a system with a single mixed flow reactor is to be much larger. Also the mixed flow reactors series has a net advantage over single CSTR for higher final sulphate concentration values, up to about 850 mg/L.

Acknowledgements

The publishing of this work was supported by a grant of the Romanian National Authority for Scientific Research –Program Nucleu PN 16 25 03 04.

References

Aubé, B & Lee, D 2015, 'The High Density Sludge (HDS) Process and Sulphate Control –Agreeing on solutions for more sustainable mine water management' – *Proceedings of the 10th ICARD & IMWA Annual Conference (GECAMIN)*, Gecamin Digital Publications, Santiago, Chile, paper 188.

Chesters, S, Morton, P & Fazel, M 2016, *Membranes and minewater – waste or revenue stream*, IMWA 2016 – Mining Meets Water – Conflicts and Solutions, IMWA, Freiberg, Germany, pp. 1310 – 1322.

Davis, ME & Davis, RJ 2003, *Fundamentals of chemical reaction engineering,* 1st Edition. McGraw-Hill Higher Education, New York.

Dietz, JM & Dempsey, BA 2002, 'Innovative Treatment Of Alkaline Mine Drainage Using Recirculated Iron Oxides In A Complete Mix Reactor', In: *Proceedings of National Meeting of the American Society of Mining and Reclamation, ASMR*, Lexington, KY, pp. 496-516.

Janneck, E, Aubel, T, Cook, M, Lantzsch, J & Widmaier, A 2013, 'Removal Of Sulphate And Heavy Metals From Mine Water - Comparison Of Ettringite Precipitation Vs. Nano Filtration In A Pilot Plant', *International Symposium „The Environment and the Industry"*, National Research and Development Institute for Industrial Ecology ECOIND, Bucharest, vol. 1, pp. 88-100.

Kastle, H & Schuster, G 1990, *Process For The Separation Of Sulfate Ions From Waste Water,* Patent EP 0250626 B1.

Levenspiel, O. 1999, *Chemical Reaction Engineering*, Third Edition, John Wiley & Sons, New York.

Meays, C & Nordin, R 2013, *Ambient Water Quality Guidelines For Sulphate Technical Appendix Update*, Ministry Of Environment Province Of British Columbia, available on http://www2.gov.bc.ca/ [20 March 2017]

Ramsay, J 2001, *Process for the treatment of effluent streams*, US Patent 6280630.