KINETIC ANALYSIS OF MANGANESE REMOVAL FROM MINE WATER - CONTINUOUS FLOW REACTION SYSTEM

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Abstract

Manganese removal from mine water by oxidation-precipitation often requires significant contact time and the use of a high pH-value for reaction stage. In order to avoid reactor over sizing or under sizing, kinetic data for manganese oxidation using mine water or very similar aqueous systems are needed. As the batch type tests can be difficult to control (e.g. to set a certain pH value during the start-up), the continuous flow reaction systems seem to be more reliable as the direct determination of reaction rate is possible in this case.

Results obtained using manganese sulphate solution and real mine water are presented here. A third order reaction rate law was obtained, taking into account homogenous and heterogeneous mechanism.

Keywords*: mine water, manganese, reaction rate*

Introduction

Often manganese is present in mine water from few ppm to hundreds of ppm and is associated with sulphate. Manganese is typically difficult to be removed from water using the conventional treatment with calcium hydroxide and aeration. Sometimes oxidizing agents are proposed. With aeration, raising the working pH above 10.0 will greatly improve the reaction rate and will also favor the precipitation mechanism, but a pH adjustment step (e.g. with HCl or better with CO_2) is to be introduced (Dinu et al 2014, Hallberg & Johnson 2005, Janneck et al 2013). Moderate pH values of 9.0 to 9.5 can be used instead, depressing the reaction rate. The rate law is to be known as it is needed for a proper reactor design.

The rate of Mn oxidation and precipitation has been found to increase with concentration of dissolved Mn and with the abundance of Mn-oxide and hydroxide surface. At a given pH and abiotic, the reaction rate is described by equation

$$-d[Mn(II)]/dt = k_1 \cdot [Mn(II)] + k_2 \cdot [Mn(II)] \cdot [MnOx] \qquad (1)$$

where [Mn(II)] is the concentration of dissolved Mn^{2+} species; $[MnO_x]$ is the surface area of Mn oxide precipitate; t is time; k_1 and k_2 are rate constants.

The Mn oxidation is autocatalytic, because precipitated solids accelerate manganese oxidation. Since the term $[MnO_x]$ depends on the reaction advance $\{[Mn]_{initial} - [Mn]_{final}\}$ the law is of second order in [Mn]. This type of equations are often referred as Stumm & Morgan dependencies (Morgan & Stumm 2005, Stumm & Morgan 1996, Means et al 2005, Von Langen et al 1997).

Batch tests can be used to obtain the kinetic law using differential or integral methods (Levenspiel 1999), but, in this case, the time needed to set a constant pH and also the time needed to filter the heterogeneous reaction mixture, comparable with reaction time intervals between samples, will lead to inaccurate results.

By using continuous flow systems, such as continuous stirred reactors (CSTR, known also as *mixed flow reactors*) it is possible to directly determine the apparent reaction rate corresponding to the working condition and to the working reactant concentration.

For an ideal stirred tank reactor operating at steady state the mass balance for constant density is (Levenspiel 1999, Davis & Davis 2003).

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

where $C_{A,0}$ is the inflow concentration and C_A is the reactor concentration for the component A, $\tau = V/Q$ is the *space-time* and $r_A(C_A)$ is the reaction rate, which is a function of C_A.

So, knowing the inlet and outlet concentration and also the flow rate and volume, the reaction rate corresponding to the outlet concentration (equal to any point in the reactor concentration, for this type of circulation) can be calculated. This will be the apparent reaction rate, as it depends on mass transfer intensity. Steady state regime is mandatory and the time required to be achieved depends on the space-time, τ.

Evaluation of the overall reaction kinetics from flow-through tests is used by some researchers (Dietz et al 2002). An experimental study has been carried out to assess manganese oxidation-precipitation reaction using model solution ($MnSO_4$) and real mine water.

Materials and Methods

The water treatment system comprised a cascade of two continuous flow stirred reactors (R1, $V_1 = 2.5$ L and R2, $V_2 = 15$ L). Each reactor reactor was equipped with mechanical mixer, 3 blades pitch blade turbine (diameter to tank equivalent diameter ratio = 0.3), variable speed n = 0-2000 rpm, medium bubble aeration difuses and with individual pH control assembly (PID) with dosing pump for lime milk. Water was pumped with a centrifugal pump Iwaki Direct Drive Pump RD-05-HCV 24-05 and the flow rate was measured by a rotameter (Figure 1).

In order to avoid non-ideality, measurements of residence time distribution were done for various mixing speed values and flow rates, using the posive step perturbation (NaCl step tracer addition) and with continuous recording of electrical conductivity which further on allows the calculation of the concentration using calibration data. This way the residence time distribution E(t) - exit age distribution and the integral residence time distribution F(t) could be appraised.

Manganese sulphate solution and the mine water were subjected to treatment using the laboratory continuous flow set-up described above.

When changing the parameters, e.g. pH, initial concentration, flow rate (to change the space-time), the system was allowed to work for at least 6 times of total system space-time to reach the new steady-state and samples were drawn from reactors, immediately filtered (0.45μm) and preserved using HNO_3. Manganese concentration was determined using AAS (Solar M6 Dual Thermo Electron).
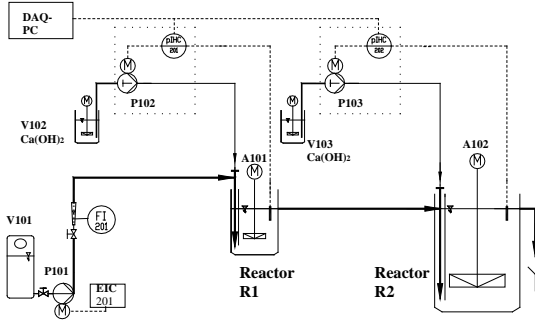
Figure 1. Continuous flow laboratory set-up

Mine water was sampled from a Romanian manganese ore mining perimeter and analyzed for the main specific chemical parameters (Table 1 and 2). This mine water is characterized by a circum-neutral pH and a low content of iron and low iron to manganese ratio (approx. 0.04 mg/mg in this case, typically 0.04 to 0.10 mg/mg according to our long term records).

Table 1 -Mine water characterization

PARAMETER	UNITS	VALUES
PH	pH units	6.5
ELECTRICAL CONDUCTIVITY	mS/cm	1.47
CCO-MN	mg O_2/L	19.3
SO_4^{2-}	mg/L	989
CL^-	mg/L	5.2
NO_3^-	mg/L	2.6
NA^+	mg/L	8.7
CA^{2+}	mg/L	153
MG^{2+}	mg/L	78.5

Table 2. Mine water characterization regarding heavy metal content

| Parameter	Units	Values	Parameter	Units	Values
Mn, *omg*	mg/L	170.5	Cr, total, *omg*	mg/L	0.373
Fe, *filtr.*	mg/L	0.074	Cr, total, *filtr.*	mg/L	0.041
Fe, *omg*	mg/L	6.10	Cu, *filtr.*	mg/L	0.043
Al, *filtr.*	mg/L	< 0.05	Cu, *omg*	mg/L	0.043
Al, *omg*	mg/L	0.201	Ni, *filtr.*	mg/L	0.646
As, *filtr.*	mg/L	<0.001	Ni, *omg*	mg/L	0.754
As, *omg*	mg/L	<0.001	Pb, *filtr.*	mg/L	0.007
Cd, *filtr.*	mg/L	< 0.001	Pb, *omg*	mg/L	0.007
Cd, *omg*	mg/L	0.0013	Zn, *filtr.*	mg/L	0.316
Co, *filtr.*	mg/L	11.917	Zn, *omg*	mg/L	0.349
Co, *omg*	mg/L	14.652			

Note: *omg* = homogenous sample; filtr. = filtered sample (0.45 µm)

Results and Discussion

Following the residence time distribution tests, we could ascertain that the flow characteristics are close to ideality for mixing speed values above 400 rpm for the two CSTR model reactors (illustrated for R1, n = 100 rpm in Figure 2 and for n = 400 rpm in Figure 3).
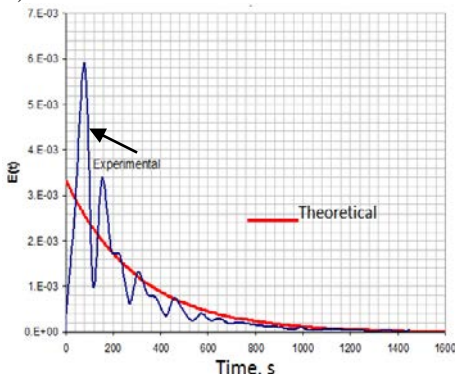
Figure 2. Residence time distribution for R1 (function E for n =100 rpm, τ = 300s)
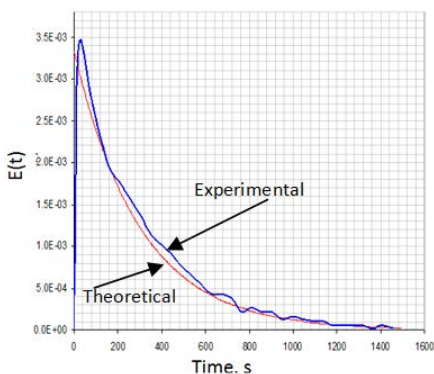
Figure 3. Residence time distribution for R1 (function E for n =400 rpm, τ = 300s)

The apparent reaction rate values were determined versus manganese exit concentration using the mass balance equation (2) for temperature t = 21°C and various pH values (8.5 to 10.0, with emphasis on pH = 9.5), while the oxygen concentration was maintained at 7 mg/L.

The best correlation representing the experimental kinetic data was found to be a third order polynomial mathematical model (equation 2),

$$-d[Mn(II)]/dt = k'_1 \bullet [Mn] + k'_2 \bullet [Mn] \bullet (k_3 \bullet [Mn]_{initial} - [Mn])^2 \qquad (3)$$

which coefficients account for:

k_1 - the contribution of homogenous mechanism,

k_2- heterogeneous mechanism catalyzed by the reaction products (manganese oxo-hydroxide), which depends on the reaction advance *([Mn]$_{initial}$ - [Mn]$_{final}$)* and also a correction coefficient k_3 for the proportion of active solid manganese species versus total manganese precipitate (non dimensional, subunit).
Equation (3) is equivalent with

$$-dX/dt = k'_2 X^3 - 2k'_2k'_3C_0 \cdot X^2 + (k'_1 + k'_2 k'^2_3 C_0^2) \cdot X \qquad (4)$$
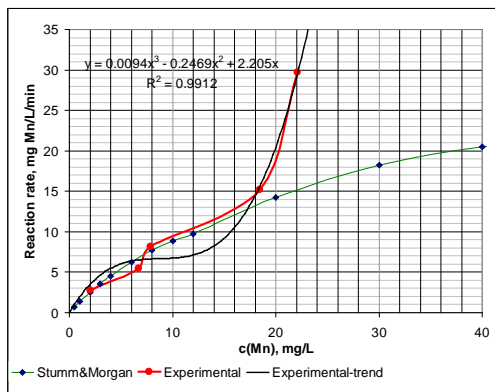
where X is the manganese concentration.

The results are shown in Figure 4 for the MnSO$_4$ model solution (2mM) and in Figure 5 for the mine water. Data were compared with kinetic data calculated using Stumm & Morgan equations, results being similar to a limited extent for low manganese concentration values.
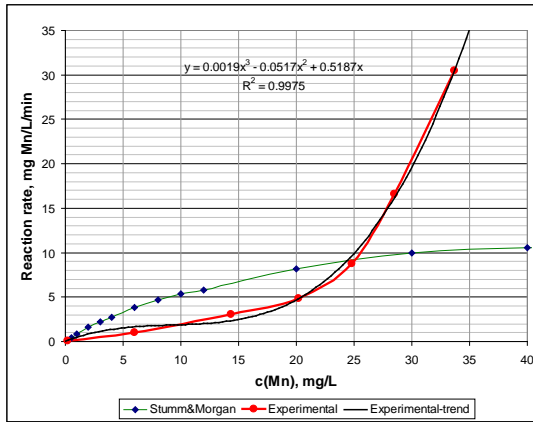
Figure 4. Reaction rate for manganese precipitation using MnSO$_4$ solution (c(O2) = 7 mg/L, pH =9.5, t = 21°C)

Reaction rate for manganese oxidation-precipitation is higher for the mine water versus the manganese sulphate solution, most probably due to higher solids formation, including manganese precipitates, but also iron oxohidroxides in the case of the mine water.

Figure 5. Reaction rate for manganese precipitation from mine water (c(O2) = 7 mg/L, pH =9.5, t = 21ºC)

The rate law obtained herein is applicable for medium manganese concentration values (tens of ppm), thus could be used to assess the volume requirements for treatment if using a reaction system containing one reactor or two CSTR in series and also plug-flow reactors, with very useful engineering results.

Conclusions

The mixed-flow reactor model was used to evaluate the kinetic rate of the manganese precipitation for model solution and for mine water. The apparent reaction rate values fit a third order polynomial mode. After further pilot level kinetic investigations for the rate law validation, the model will be used for mine water treatment reaction systems on higher level. It can be recommended to establish rate laws using onsite continuous pilot level trials for any mine water source, because of strong dependance on the reaction rate to specific factors, including iron content, iron to manganese ratio and also because of the availability of mine water with real temperature.

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