SHORT COMMUNICATION

MATHEMATICAL MODELLING FOR MAGNETITE (CRUDE) REMOVAL FROM PRIMARY HEAT TRANSFER LOOP BY ION-EXCHANGE RESINS

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ABSTRACT. The present research focuses to develop mathematical model for the removal of iron (magnetite) by ion-exchange resin from primary heat transfer loop of process industries. This mathematical model is based on operating capacities (that's provide more effective design as compared to loading capacity) from static laboratory tests. Results showed non-steady state distribution of external Fe^{2+} and limitations imposed on operating conditions, these conditions includes; loading and elution cycle time, flow rate, concentration of both loading and removal, volume of resin required. Number of generalized assumptions was made under shortcut modeling techniques to overcome the gap of theoretical and actual process design.

KEY WORDS: Magnetite, Mathematical modeling, Ion-exchange resin, Operating capacity, Loading capacity

INTRODUCTION

In water systems of power plants, there is slow corrosion of the interior metal surfaces of the primary coolant. This corrosion products become activated by neutron flux from the fission reactor, or other chemical reactions of process industries when pass through reactor. Some of these activated corrosion products are removed by the reactor's water system (i.e. by filters, membranes, etc.) but a small amount is continually deposited/dissolved on the primary coolant system's internal surfaces [1, 2]. Once activated corrosion products are deposited, they are not removed by the reactor water cleanup system and continue this accumulation [3]. Also as a direct accumulation of crude, radiation level in the vicinity of the primary system rises and affects heat recovery.

In process plants, ferrous metals are mostly used in primary piping system. Ferrous metal (steel) can be made as anti-corrosive as stainless steel by the building up of a black oxide layer, known as magnetite, on its surfaces exposed to high temperature water. The reaction at high temperature water and iron is shown in equation 1. And below 450 °F and above 300 °F the reaction probably proceeds as shown in equation 2 and 3, respectively.

$$FeO + Fe_2O_3 \longrightarrow Fe_3O_4 \,(magnetite) \tag{1}$$

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + 2H_2O + H_2 \tag{2}$$

$$3FeO + H_2O \longrightarrow Fe_3O_4 + H_2 \tag{3}$$

Under adverse conditions the oxide layer is broken down and chemical attack can take place at increasing rate. Ferrous metal (steel) can be made as anti-corrosive as stainless steel by the building up of a black oxide layer, known as magnetite, on its surfaces exposed to high temperature water [4]. This crude released to the water can create several problems like, accumulate in lines causing reduction in flow rates, cause wear and malfunction of moving

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parts, may be deposited on fuel element surfaces, causing a change in heat transfer properties, can be activated neutron flux and deposited on out-reactor parts of the system causing radiation problems, etc. Previously many strives have been made to remove crude by filtration, membranes, etc. but they will not become fruitful, owing to frequent choking problem and economical prospective. Thus we think that, ion-exchange is the better option in continuous flow process for magnetite removal, easily regenerated and its modeling gives proper idea to process design engineers for its utilities.

EXPERIMENTAL

Experimental setup is designed to test for wide range of loading capacities for ion-exchange resins [4]. These experiments were separately carried out for cation and anion resins and formation of matrix solution was also made separately for cation and anion resins. Experimentation involved following steps: (i) charging/regeneration of 50 mL cation and anion resin, with 4 % H_2SO_4 or 4 % NaOH solutions, respectively; (ii) washing of resin with makeup water; (iii) formation and passing of matrix solution; and (iv) washing of resin with makeup water and then again loading of matrix solution.

AMBERLITE IRA 120 Na gel type strongly acidic cation exchange resin (sulphonated polystyrene type) of 1.25 meq/mL exchange capacity and 20 % swelling margin was used [7]. AMBERLITE IRA410 Cl is a premium grade strongly basic anion exchange resin of 1.35 meq/mL exchange capacity, based on cross-linked polystyrene, and was used in current experimentation [8]. Both resins of 0.75 effective sizes were made by Rohm and Haas Company, USA. Matrix solution of crude Fe (iron) is taken in the form of magnetite (Fe_3O_4), and prepared in 1 L makeup water with; 0.2 % EDTA = 2 g, 0.18 % citric acid = 1.8 g, 0.01 % hydrazine = 0.1 mL and 0.01 % rodine = 0.1 mL. EDTA dissolved the Fe, citric acid helps EDTA to make complex with Fe. Hydrazine is used as oxygen scavenger and rodine is used as corrosion inhibitor. Then this solution was heated on hot plate at 60-70 ^{o}C for two hours with continuous stirring, and filtered. Then the magnetite was weighed at filter paper (by measuring the weight difference of magnetite initially dissolved and magnetite on filter paper and the magnetite or iron dissolved in matrix solution was calculate. Then pH and conductivity of matrix solution before passing through resin was checked.

Study of cation resin (IRA-120). 700 mL of 4 % H_2SO_4 solution was loaded on 50 mL resin with flow rate of 1.5 mL/s. Online measurement of pH indicates about resin charging, and then washed with 1900 mL makeup water. The concentration of H^+ was high first in makeup water, while it decreases with the passage of time, showed that, pH of first sample was low while it was high of later samples. 500 mL sample of matrix solution was allowed to pass through cation resin (IRA-120) of 91 mg dissolved magnetite. Therefore, the Fe dissolved in matrix solution was 0.72 x 91 (as Fe is 72 % by weight in magnetite) = 65.66 mg. pH of matrix solution before passing through cation resin was 2.38 and conductivity of matrix solution before passing through cation resin was 3.63 mS. And total Fe loaded on cation resin (50 mL) was 21.56 mg (Figure 1). Fe loading in resin is decreasing (except first and last readings because makeup water is included in these readings) with passage of time. The reason is clear because with passage of time, the sites available to load Fe are decreasing.
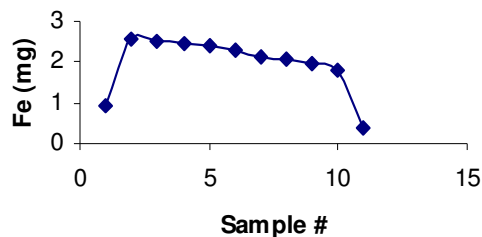
Figure 1. Fe loading in cation resin after each sample.

Then regeneration of cation resin (IRA-120) is done again with 4 % H_2SO_4 solution as previously and total Fe unloaded by 4 % H_2SO_4 solution (500 mL) was 2.49 mg. The 4 % H_2SO_4 solution did not deloaded whole iron because of high flow rate through resin provide less contact time to exchange and owing to low concentration of H^+ in solution. Then washing was done with 2000 mL of makeup water of conductivity 4.01 uS and pH variation showed washing activity (Figure 2). Total magnetite in matrix solution was 270 mg but only dissolved 81.9 mg. Therefore Fe dissolved in matrix solution was 0.72 x 81.9 (as Fe is 72 % by weight in magnetite) was 59 mg loaded.
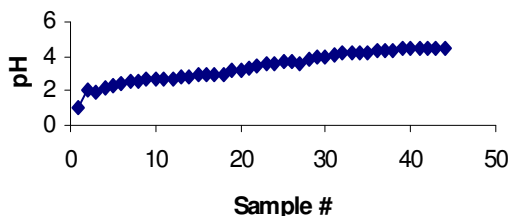

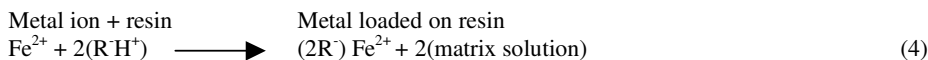Figure 2. pH variation with sample number.

Study of anion resin (IRA-410). Same volume of anion resin (50 mL) was used as for cation resin and charged with 500 mL of 4 % NaOH solution of pH 12.92, with flow rate of 1.55 mL/s. pH variation showed charging of resin. Then 500 mL of matrix solution containing 57 mg Fe, of pH 2.35 and conductivity 3.07 mS, was alloed to pass with flow rate of 1.5 mL/s, the total Fe loaded by anion resin was 54.83 mg. Then again regeneration process was repeated with 4 % NaOH and all operating parameters were noted. Also washing practice was repeated with 2000 mL makeup water at lower flow rate of 1.35 mL/s and pH fall was recorded. After regeneration the anion resin was loaded almost the same amount of Fe as before regeneration.

Study of mix-bed resin. Charging and washing of mix-bed resin (50 % cation and 50 % anion resin) was already done during experiments of cation and anion resins, however their regeneration was not performed together. So, there is only one additional step involved in this experiment. Same procedure was repeated for mixed bed and total Fe loaded was 25.93 mg under identical conditions.

MATHEMATICAL MODELLING

The behavior of ion exchange resin towards iron loading is mathematically unsteady with respect to time [9]. Initial conditions in a bed are not uniform in industrial practice and

complexity of calculations is thereby even further increased. In majority of cases; to obtain the parameters needed to model the breakthrough and elution curves, Langmuir and Freundlich models were used to fit adsorption isotherms data and numerical optimization was applied to calculate mass transfer coefficients [9]. The performance of exchanger for divalent ions is always greater than theoretical equilibrium constant [7, 8]. The shape of breakthrough curve does not change with the length of resin bed [10]. The general reaction described in equation 4.

Metal ion + resin   Metal loaded on resin

$$Fe^{2+} + 2(R^-H^+) \longrightarrow (2R^-)\,Fe^{2+} + 2(\text{matrix solution}) \tag{4}$$

When monovalent ions are replaced with the divalent ions, each new counter ion balances two charged sites in the resin shown in equation 5 and rate constant shown in equation 6.

$$Fe^{2+} + 2NaR \longrightarrow FeR_2 + 2Na^+ \tag{5}$$

$$K' = [(CNa^+)^2 \times CFeR] / [CFe^{2+} \times (CNaR)^2] \tag{6}$$

With simplified assumptions like, no resin flow in fixed bed system, so UR or R set to zero, constant pattern in fixed beds, no axial dispersion or back mixing, so some or all of the coefficients EL, ER, λ and σ are set to be zero. Steady–state operation of counter flow systems, so differentials with respect to time or set to zero. Rate coefficients are independent of concentration. The following expression based on the Fe^{2+} ion balance in the liquid phase was adopted, without take into account the axial dispersion expression shown in equation 7.

$$X = -v\,\partial X / t\,\partial\,z + k_1 a\,(X-X^*) / \varepsilon \tag{7}$$

with initial condition: X = Fe initial for t > 0   0 < z , Z
and boundary conditions: X = Fe conc.   for t = 0   z = 0

where z is the distance from the considered point until the bed inlet, ε the bed porosity and t the feed time, X is the Fe concentration in the liquid phase and X^* the Fe^{2+} concentration at equilibrium. The generalize expression will made for the calculation of resin volume with respect to the concentration of Fe present in feed can be calculated from equation 8.

$$\text{Volume of resin in mL} = \text{Fe in mg/L} \times 72 \tag{8}$$

The mathematical expression for the Fe^{2+} loading and unloaded on experimental basis, in equation 9 and 10, respectively.

$$dy/dt = -0.23 \times dx/dt + 1.22 \tag{9}$$

$$dS/dt = 0.02\,P\,dp/dt - 0.11 \tag{10}$$

The resolution of the system describing the elution curve was also achieved by discrediting the spatial variable and solving the ordinary differential equations system by the same algorithm of the loading step [11, 12].

CONCLUSIONS

The great benefit from this shortcut modeling on operating condition can integrate the design to overcome the gap of theoretical and actual process design, and impede the implementation of the successful application on commercial scale designs of ion-exchange processes. The results shown include the non-steady state distribution of extracted Fe^{2+} and limitations imposed on operating conditions to make the model steady state. For hydro metallurgical plants where sequential ion exchange systems and other continues operations, the model is very helpful in design choices. The proposed model has following significant features: (i) the process flow

specifications such as Fe concentration, flow rate, operation time, for both loading and elution (regeneration) program; (ii) resins based physical specifications such as bed volume with respect to concentration of Fe in feed, i.e. direct indication of mass balance across the ion exchange bed; and (iii) process control strategies according to resin specifications like temperature, pressure, flow rates, and effects of operating parameters on exchange phenomena.

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