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O. J. Gregory[a]; S. M. Barnett[a]; F. J. Deluise[a]
[a] DEPARTMENTS OF CHEMICAL ENGINEERING AND MECHANICAL ENGINEERING, UNIVERSITY OF RHODE ISLAND KINGSTON, RHODE ISLAND

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Manganese Removal from Water by a Precipitate Flotation Technique

O. J. GREGORY, S. M. BARNETT, and F. J. DELUISE

DEPARTMENTS OF CHEMICAL ENGINEERING AND MECHANICAL ENGINEERING
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND 02881

Abstract

Microgas dispersions were used to remove manganese from dilute aqueous solution by a precipitate flotation technique. Manganese in its coagulated oxide form is difficult to remove from water by other methods, such as filtration. Flotation processes appear to be more suited to continuous manganese dioxide removal than other conventional methods. Taking advantage of the tendency for manganese dioxide to coagulate, manganese removals as high as 98% were observed for continuous flotation when the metal was present in only trace quantites (2 to 5 mg/L).

INTRODUCTION

For many industrial and domestic uses, manganese has been an undesirable metal in water even in trace amounts (*1*, *2*). Manganese concentrations in potable water supplies exceeding 0.05 mg/L can subsequently lead to coloration and turbidity problems (*1*, *3*). Because water supplies previously considered unusable are now being reassessed due to greater demand, the control and removal of manganese to within this limit must be achieved. Historically, this has been done using an oxidation–precipitation process followed by filtration.

A method of removal that has not been previously considered for manganese removal is flotation, particularly precipitate flotation (*4–6*). In precipitate flotation, small bubbles stabilized with surface-active agents carry the precipitated particles, attached by coulombic forces, to a surface where the particles concentrate for easy removal. Separation efficiency is determined by surface area available for solute–particle attachment and by charge compatibility of the bubbles with the solute.

The use of microgas dispersions (MGD) as a means of increasing flotation efficiency by increasing the available surface area has only been recently considered (*7–9*). Microgas dispersions are collections of small bubbles (1 to 50 μm in diameter) linked together and distributed in an aqueous medium. The dense packing of the small bubbles in the dispersion allows the dispersion to have surface area to bulk volume ratios as large as 5×10^3 cm^2/cm^3. Other properties and advantages of microgas dispersions are discussed in previous papers (*7–9*).

Microgas dispersions used in this study were first manufactured by Sebba (*7*) using a modified Venturi device, shown in Fig. 1. Gas is introduced into a constricted region of low pressure and high fluid velocity, becoming entrained in the fast-moving stream forming the dispersion.

In precipitate flotation an ionic species is concentrated from aqueous solution by forming a precipitate which is subsequently removed by flotation. The completeness of removal is dependent on the extent of the

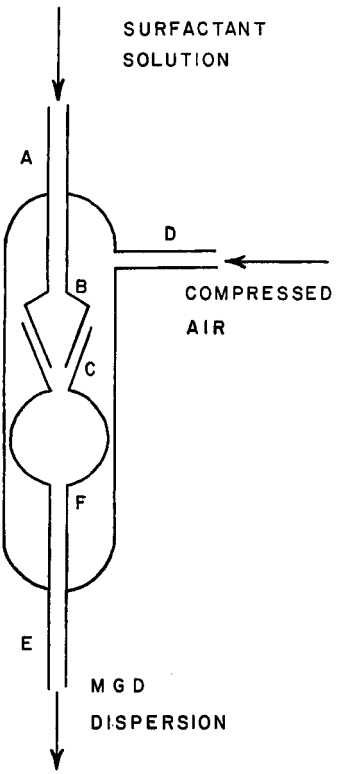

FIG. 1. Schematic of the device used for the production of MGD dispersions.

two controlling mechanisms: the degree to which the metal is precipitated as the hydroxide or oxide, and the degree to which this is floated. The surfactant in precipitate flotation must carry out three functions: (a) wet the surface of the particles, (b) produce a foam capable of supporting precipitated particles, and (c) promote interaction between the particle and the gas bubble interface (*10*). The flotation technique described in this paper differs from conventional precipitate flotation in that the bubbles are not produced from within the contaminated solution. In this technique the bubbles can be generated at one location and pumped to another location without changing the properties of the dispersion. However, it is believed that many of the same functions and interactions of the surfactant molecules still affect the separation.

The modified flotation technique described here using bubbles generated external to the contaminated solution is dependent on the following: (a) pH of the solution, (b) surfactant molecule charge and charge density, (c) surfactant concentration, (d) dispersion stability, and (e) dispersion addition rate. Effective separation can be facilitated in either a batch process (single burst of dispersion) or in a continuous process since the physical properties of the MGD dispersion are such that once generated they can be easily pumped. In a batch separation the bubbles in the MGD dispersions allow more contacting of the precipitated particles in the solution so they can be removed in a shorter period of time than in conventional flotation. This is because the bubbles in the dispersion are joined together to form a network of bubbles which rises with the velocity of single, larger bubbles.

In the continuous separation of the precipitated particles, the same phenomenon is observed. However, in this process the dispersion and contaminated solution streams enter at opposite ends of the separation column and move countercurrently through the column to effect separation. It is believed that the network of bubbles simulates a moving filter bed where fresh surfaces are continually becoming available for impingement of the precipitated particles. The bubbles then carry the particles to the top of the column for easy removal.

EXPERIMENTAL APPARATUS

The generator used in this study for the production of MGD dispersions is shown in Fig. 1. It incorporates a Venturi device first used by Sebba (*7*) to produce the MGD. The recirculation of the surfactant solution and dispersion mixture is critical to the formation of a stable MGD.

The liquid mixture enters the Venturi shown in Fig. 1 at A at a rate of 10 L/min and enters the constricting region at B. At the same time, air

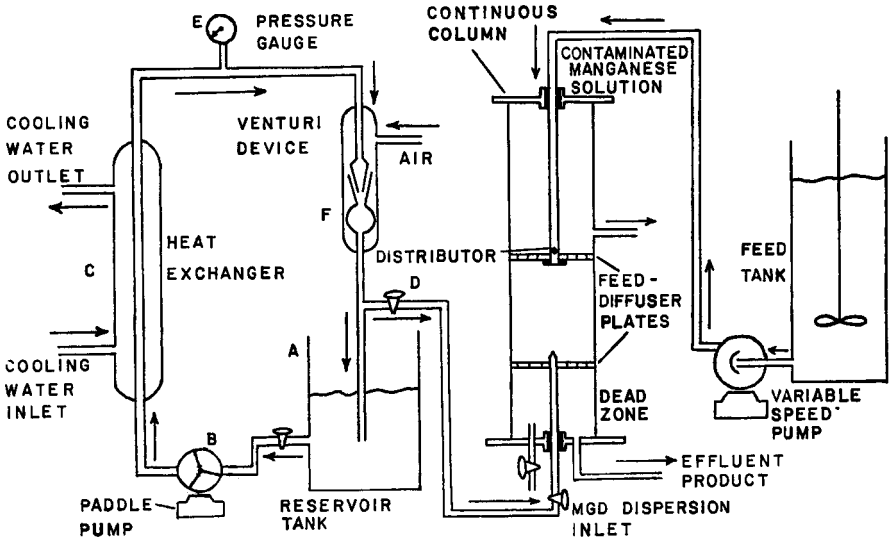

FIG. 2. Flow plan of the continuous process used for the removal of manganese.

under a slight positive pressure enters at D. Air flows into the gap between the constricting surfaces C and B and becomes entrained to form the MGD dispersion. The proper level of the liquid phase in the Venturi is maintained by regulating the air pressure at D. Support apparatus was incorporated to maintain and monitor steady-state conditions. The flow scheme used to insure steady-state conditions is shown in Fig. 2. The operation of this system is as follows: surfactant solution in reservoir tank A is gravity fed to paddle pump B where it is pumped through heat exchanger C to maintain the temperature at 25°C. The solution leaving the heat exchanger enters generator F to form an MGD which can be withdrawn on demand by opening valve D. The pressure of the system is monitored by a gauge at F. A relatively large tank was used as the reservoir so that during steady-state operation the product could be withdrawn without upsetting the system. In addition, the containers for the entire system were transparent, enabling a visual inspection of the operation.

Batch flotation experiments were carried out in a cylindrical glass column 60 cm in height and 7 cm in inner diameter. A side port was constructed ~7 cm from the base of the column to facilitate the sampling of the bottoms product.

Continuous flotation experiments were carried out in a glass column designed specifically to accommodate the countercurrent flow of contaminated solution and MGD dispersion. The column measured 5 ft in height and 0.5 ft in inner diameter. Adjustable feed-diffuser plates were used.

To accommodate these adjustable plates, a number of side stream ports were afixed to the column. These ports were 0.5 in. in inner diameter and were spaced 3 in. apart from each other. The feed plates were designed to accommodate the bouyant MGD rising through the column to allow intimate contacting of the feed while distributing the contaminated solution. To accomplish this, a large number of 1/4 in. holes were made in the horizontal feed plates throughout the entire cross section. The lower feed plate also served as a device to establish a dead zone in the bottom of the column, inhibiting any short circuiting of the bubbles as the product was withdrawn.

PROCEDURE

In the batch flotation runs the column was filled with a liter of a manganese solution and oxidized with a dilute solution of sodium hypochlorite at various pH's. A burst of MGD was then introduced into the column. An initial sample was taken prior to each run and a final sample was taken after the dispersion had risen to the surface of the column at the end of the run. Two variables were defined to characterize each run on a common basis. Dilution factor (original volume of liquid to be treated/final volume) was used as an indication of the amount of dispersion added to the untreated solution to affect separation, and percent removal was used as an indication of the degree of removal or efficiency of the separation.

In the continuous flotation experiments the active column height for mass transfer was predetermined. The flow rate of the manganese feed solution was selected and controlled by means of a variable speed pump. The column was filled with the feed solution at the predetermined flow rate. The MGD dispersion was then fed to the column as shown in Fig. 2 and the flow rate was adjusted so that steady-state conditions were reached. Steady-state conditions were reached when the bottoms concentration of manganese remained constant with respect to time or $d(\mathrm{Mn})_b/dt = 0$. Bottom samples were taken throughout the course of the run at regular intervals to determine the concentration of the bottoms as a function of time. Initially, samples of the feed were taken to determine its concentration.

Solutions containing approximately 2.5 and 5.5 mg/L of manganese were used throughout the study. Manganese is soluble or partially soluble depending on the pH of the solution and amount of oxidizing agent present. Sodium hypochlorite was used as the oxidizer in all cases. A stock solution of manganese sulfate was prepared according to standard methods and procedures (*1*). This solution was then diluted to the desired

concentration with distilled-deionized water. Following dilution, the solution was oxidized with sodium hypochlorite (3×10^{-4} L NaOCl/L solution). This concentration of sodium hypochlorite is approximately five times the theoretical requirement to completely oxidize the manganese. In this way, complete oxidation of the manganese would be insured at a given pH. The pH of the untreated solution was adjusted using 5 N NaOH and 1 N HCl and was measured with a pH meter.

ANALYTICAL METHOD

Atomic absorption spectroscopy enables the direct determination of aqueous solution concentrations with acceptable accuracy and, therefore, was the method of choice (*1*). Standard solutions of known concentrations were used to determine the concentration of the unknown. A Perkin-Elmer atomic absorption spectrophotometer was used for all determinations.

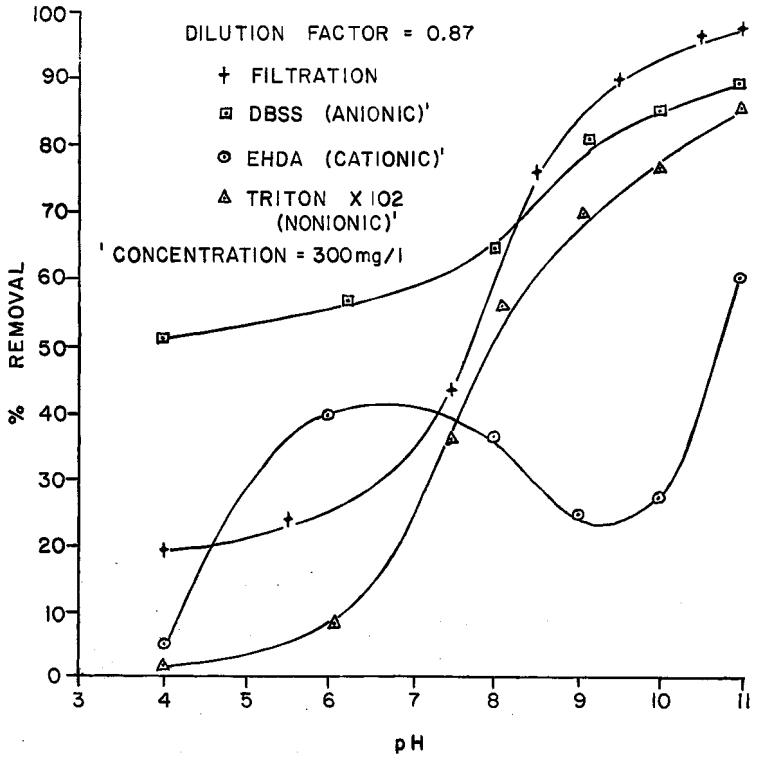

FIG. 3. Effect of pH on the removal of manganese (2.5 mg/L) using MGD dispersions made with various surfactants.

RESULTS AND DISCUSSION

The results of the batch runs using various surfactants are shown in Fig. 3. Since pH determines manganese solubility and the surfactant determines the charge on the bubble surface and the charge density, the controlling mechanism becomes obvious from the graph. The filtration curve in Fig. 3 gives some indication as to which mechanism is the controlling one, either ion or precipitate flotation, since this curve is actually a solubility curve. These data were obtained from experiments involving the precipitation of manganese and subsequent filtration. Literature values for the IEPS (isoelectric points) of the stable manganese oxide hydroxide precipitates in the pH range of interest are as follows (*11*): $IEPS_{Mn(OH)_2} = 7.0$ and $IEPS_{MnO_2} = 4$ to 4.5. The influence of adsorbed cations and anions on the removal of the precipitate based on these IEPS values indicates that MnO_2 was the stable species. The absorbed cations

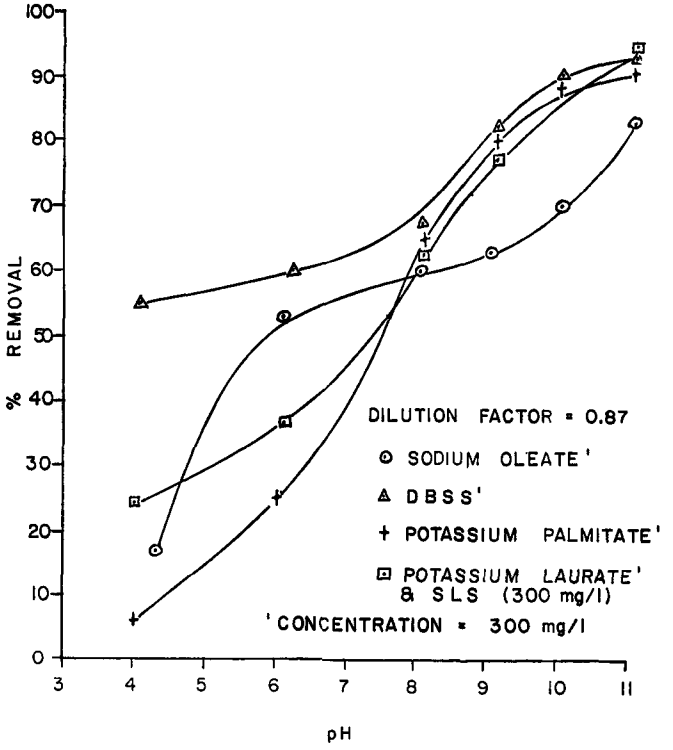

FIG. 4. Effect of pH on the removal of manganese (2.5 mg/L) using MGD dispersions made with various anionic surfactants.

were responsible for the enhanced removal at pH = 8, and their effect is evident when comparing the other surfactants and filtration curves in this pH range.

From Fig. 4, the anionic surfactant dodecylbenzene sodium sulfonate (DBSS) proved to be the most efficient in removing manganese in the precipitate flotation region of pH greater than 7.0. With small additions of MGD dispersion (dilution factor = 0.87), removal efficiencies as high as 90% were observed for this surfactant. Below a pH of 8.0, there was considerable removal of the manganese even though a large portion of it had not precipitated. Apparently this surfactant has some potential as a candidate for ion flotation, since appreciable removals were observed in the pH region where the manganese is in ionic form. A complex formation is also possible in this region.

Of the anionic surfactants investigated, DBSS was the most efficient in removing manganese over the pH range of interest. It can be inferred that DBSS exhibited an optimum balance, having sufficient attractive forces (strong coulombic forces) to maintain particle attachment with sufficient surface activity to stabilize the bubbles of the MGD to support the precipitated particles. The removal of manganese from solution is attributed to the physical entrapment of particles and the ionic coupling of the manganese particles. A residual positive charge due to excess Mn^{4+} ions causes the particles to react with the surfactants' sulfonate groups which cover the surface of the bubbles. A high surface activity aids in the spreading of surfactant on the particles, thereby promoting the coverage of the reactive groups.

The physical properties of the MGD are such that they can be incor-

TABLE 1

Data for the Continuous Removal of Manganese

Run	Dilution factor[a]	Initial[b] Mn conc (mg/L)	Final Mn conc (mg/L)	Plate separation (cm)	Bottoms flow rate (L/min)	% Removal
1	0.68	5.5	0.11	11	1.5	96
2	0.66	5.2	0.06	9	1.2	98
3	0.78	5.8	0.06	23	2.0	98
4	0.79	5.8	0.11	38	2.4	95
5	0.80	5.2	0.17	23	2.4	95
6	0.66	2.5	0.20	23	2.0	94
7	0.70	2.5	0.08	9	1.5	94
8	0.77	2.6	0.08	38	1.8	95
9	0.80	2.4	0.14	23	1.7	93

[a]Surfactant: DBSS (300 mg/L).
[b]pH = 10.5.

porated into a continuous countercurrent process without adversely effecting particle–bubble attachment and bulk fluid flow. Greater removals can also be expected from the improved mass transfer associated with countercurrent separation due to the continual renewal of fresh surfaces for particle attachment. The results of the continuous runs are presented in Table 1. In all cases, removal was greater than 90%.

In Fig. 5, the effect of MGD dispersion rate on removal is shown. Removal was observed to be nearly constant over the entire range of dynamic dilution factors investigated, indicating that removal was independent of how much dispersion was used relative to the amount of solution treated. This suggests that other mechanisms were controlling the removal of manganese in the continuous process. Fig. 6 shows the effect of flow rate on mass transfer. Using a dimensional analysis of the governing parameters, mass transfer was postulated to be a function of flow rate. A linear dependence on flow rate is observed when plotting is on a rectangular scale. The linear dependence on flow rate observed

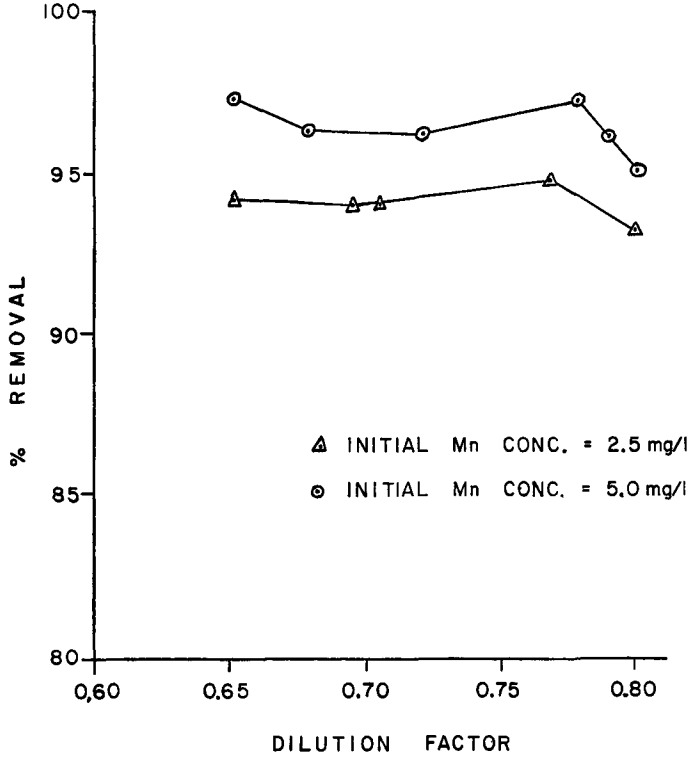

FIG. 5. Effect of dilution factor on the continuous separation of manganese.

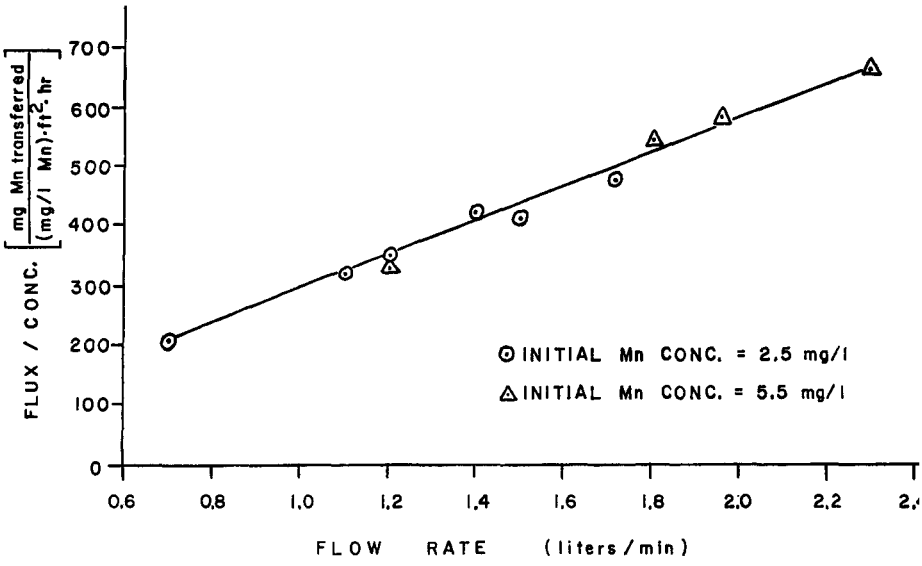

FIG. 6. Correlation of normalized manganese flux and volumetric flow rate in the continuous column.

suggests that transfer occurs via an impingement mechanism as in filtration or in dust collection, where the amount of material transferred is highly dependent on the flow rate of the stream carrying the suspended particles. It is believed that in this case the bubbles form a coherent matrix where they are linked together in such a way that the dispersion simulates a moving filter bed rising through the column with a velocity that is dependent on the flow rate of the contaminated solution entering at the opposite end of the column. It is known that MGD dispersions do not have rise velocities associated with micron-sized bubbles but do have ones associated with the total number of bubbles comprising the matrix.

Also, the removal of manganese was not affected by small changes in MGD dispersion flow rate or by small changes in the MGD dispersion quality which varied between 45 and 50% air by volume for the continuous runs. Because of this apparent lack of dependence on flow rate of MGD, an H.T.U. analysis was attempted to correlate separation data with active column height. It was not applicable to this system, since equilibrium data were meaningless due to the irreversibility of the separation. Once the dispersion affected separation and the air left the system as the foam collapsed, air could not be added to the separated mixture in an attempt to duplicate the separation due to the loss in efficiency from surface area considerations.

The aforementioned dimensional analysis yielded a linear relationship between mass transfer and flow rate:

$$k = 5V$$

where k = mass transfer coefficient (mg Mn/ft^2.hr) and V = volumetric flow rate (L/min).

The mass transfer coefficients determined over the range of manganese solution feed rates studied were between 500 and 3850 mg Mn/ft^2. hr. The column was also capable of treating up to 2.3 L/min of incoming Mn solution using only 23 cm of active column height (4.2×10^{-3} m^3 apparent bed volume). If an active bed volume of 1 ft^3 is considered for scale-up purposes, this continuous scheme would be capable of processing 14.9 L/min of manganese solution containing about 5.5 mg/L manganese. By comparison, if a similar solution were treated by a pressure filtering process which used a 1 ft^2 diatomaceous earth filter with a 30

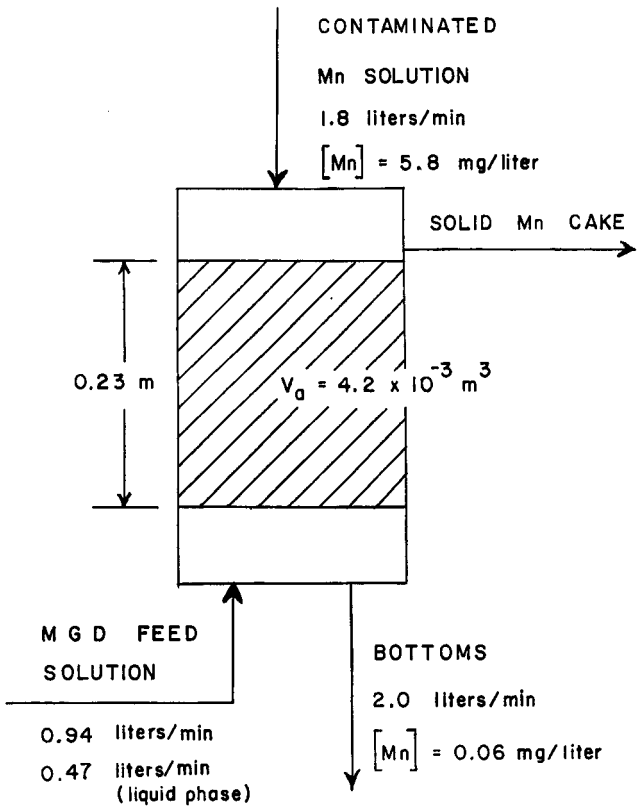

FIG. 7. Continuous countercurrent separation scheme.

psi pressure drop, only 4 L/min could be processed. A material balance providing typical flow rates and concentrations that could be expected from a separation using the continuous countercurrent flow scheme is shown in Fig. 7. In terms of absolute reduction in manganese levels in the contaminated streams fed to both the batch and continuous columns, the following reductions were attained in relation to MGD consumption. Manganese was reduced from an initial concentration of 5 mg/L to a final concentration of 0.2 mg/L using an addition rate of 3×10^{-1} L MGD/L contaminated solution in a batchwise flotation. For the continuous separation process, manganese was reduced from an initial concentration of 5.5 mg/L down to a final concentration of 0.06 mg/L using an addition rate of 2.6×10^{-1} L MGD/L contaminated solution. It appears that some critical addition rate must be achieved before the separation efficiency required to make the method feasible is realized. This critical addition rate for the Mn system studied is on the order of 3×10^{-1} L MGD/L solution regardless of the nature of the process.

CONCLUSIONS

Manganese was removed from solution most efficiently using MGD dispersions made with anionic surfactants, particularly DBSS. The use of these surfactants in the precipitate region (pH = 8 to 12) for manganese resulted in its easy removal, evidenced by the charge compatibility between surfactant and precipitate particle and by the extent to which the manganese in solution formed a stable precipitate. In the case of the batch process for the removal of manganese, 80% of the separation was complete within 5 min, making such a process much more attractive than other conventional batch processes, such as flocculation and sedimentation, from the viewpoint of reduced residence time. Also, MGD batch flotation requires no pretreatment of the contaminated solution with surfactant prior to aeration as does conventional flotation. MGD flotation requires only the direct addition of dispersion to the contaminated solution to effect separation. A certain flexibility is also incorporated into the system, since MGD dispersions can be generated at one point and pumped to another. The main advantage, though, is the increased surface area available for particle–bubble interactions (orders of magnitude greater than conventional flotation) made possible by the large amounts of air entrained in the Venturi generator to create the MGD dispersion.

However, the most dramatic gains in removal are realized for the continuous removal of manganese. A continuous countercurrent scheme was designed which successfully reduced the manganese present in solution to a final concentration of 0.06 mg/L continuously. The low levels

of manganese in the effluent streams that were attained approach the maximum acceptable limit for manganese in drinking water set by the U.S.P.M.S. (*12*) at 0.05 mg/L. Such low levels are also indicative of the potential this removal method has, since the absolute attainable concentrations are approximately equal to those of other continuous methods (*1–3*).

A summary of the main conclusions of this study on the continuous separation of manganese follows. (a) The autocatalytic oxidation of manganese promoted the coagulation of manganese dioxide and thus aided its removal by forming larger precipitate particles which made bubble attachment and impingement easier and the physical-chemical absorption more efficient. (b) The effectiveness of the process depended primarily on the surface activity of the MGD solution, the physical impingement of the particles in the bubble matrix, and the coulombic attraction between oppositely charged particles and surfactant groups to insure attachment until the separation was complete. (c) The renewal of fresh surfaces for absorption and impingement in the countercurrent flow scheme resulted in substantial improvements in removal efficiency compared with those of batch flotation.

There are several practical advantages that this continuous process has over more conventional continuous processes such as filtration. One advantage is that the pressure drop normally encountered from the head loss through the filter cake is eliminated. With the Venturi generator there is essentially no pressure drop through the generator and the only pressure drop in the column is the head from the water level in the column. This eliminates short run times and downtime, and lowers pumping costs. Also, the only waste being discharged from the column is a solid cake of precipitated manganese dioxide and spent surfactant. Handling problems can be eliminated by making provisions to contain the froth which is laden with manganese as it forms on the surface of the column of water. By incorporating an overflow with a mechanical foam breaker into the system, the manganese and surfactant cake can be collected as the foam collapses.

Overall, the method presented here for separating finely divided particulates from aqueous solution has a great deal of potential not only for water treatment applications, but for wastewater treatment applications as well, since the basic technique and approach can be applied to a variety of other metal systems.

Acknowledgments

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