01 Jan 1985

Removal Of Colloidal Silica In Simulated Seawater By A Dynamic Multi-Short-Circuited Galvanic Cell

Jan E. Osterholm

Paul W. Kramer

Hlrotsugu K. Yasuda
Missouri University of Science and Technology, yasudah@mizzou.edu

Recommended Citation

J. E. Osterholm et al., "Removal Of Colloidal Silica In Simulated Seawater By A Dynamic Multi-Short-Circuited Galvanic Cell," *Industrial and Engineering Chemistry Product Research and Development*, vol. 24, no. 3, pp. 468 - 473, American Chemical Society, Jan 1985.
The definitive version is available at https://doi.org/10.1021/i300019a027

Schwartz, A. B. U.S. Patent 4 174 272, 1979.
Venuto, P. B.; Hamilton, L. A.; Landis, P. S. *J. Catal.* **1966a**, *5*, 484.
Venuto, P. B.; Hamilton, L. A.; Landis, P. S. *J. Catal.* **1966b**, *6*, 253.
Venuto, P. H.; Hamilton, L. A.; Landis, P. S.; Wise, T. T. *J. Catal.* **1966c**, *4*, 81.
Zhdanov, S. P. "Some Problems of Zeolite Crystallization"; American Chemical Society: Washington, DC, 1971; Adv. Chem. Ser. 101.

Received for review September 5, 1984
Revised manuscript received February 19, 1985
Accepted March 16, 1985

Removal of Colloidal Silica in Simulated Seawater by a Dynamic Multi-Short-Circuited Galvanic Cell

Jan-E. Osterholm, Paul W. Kramer, and Hirotsugu K. Yasuda*

Graduate Center for Materials Research, University of Missouri—Rolla, Rolla, Missouri 65401

A dynamic multi-short-circuited galvanic cell (MSCGC) with Pt–Al electrodes has been used to study the removal of colloidal silica from seawater as a pretreatment step for the desalination of seawater by use of reverse osmosis. The rate of silica removal is observed to be affected by the flow rate of the solution through the cell and the dissolved oxygen content of the solution as well as by the nature of the aluminum electrode surface and the number of contact points (short circuits) between the aluminum and platinum. The total silica content is reduced by 95% by use of this cell configuration.

Introduction

In order to avoid membrane fouling during the reverse osmosis desalination of seawater or brackish water, it is important to remove effectively the membrane-fouling substances. unlike heavy contaminants and those which float, colloidal materials cannot be easily removed by conventional mechanical methods, e.g., filtration, settling, etc. These membrane-fouling substances are (Liss, 1975): (a) inorganic suspended solids and colloids, such as silica, talc, quartz, floc of oxidized iron and manganese, calcium sulfate, and carbonate (scale-forming constituents when their solubility limits are exceeded) and (b) organic nutrients which promote biological growth on membrane surfaces (such as polysaccharides, phosphates, proteins, and lipids).

Colloidal silica was selected as a suitable model for the inorganic colloids that are capable of fouling reverse osmosis membranes for the following reasons. Silicon in seawater is found in solution as silicate ions, in suspension as silicon dioxide, both free and in diatoms and other living organisms, and as clay minerals. Its amount is affected by geochemical and biological events and shows a wider range of variation than that of any other element (Armstrong, 1965).

Coventional methods of treating raw water include lime softening and coagulation followed by filtration. The coagulation or flocculation process to remove colloidal materials from water is ancient, dating to the Egyptians's use of almonds, beans, and alum as coagulators to clarify muddy water (Powell, 1954). The process of coagulation involves the addition of certain soluble metallic salts to the water whereupon coagulation takes place and gelatinous substances or flocs form. These then agglomerate to form larger flocs which can be removed by sedimentation or filtration.

The principal role of the coagulant is to provide highly charged ions that will neutralize the electrical charges of the colloidal material, causing it to precipitate. Many materials are capable of coagulating suspended solids and colloids; however, aluminum and iron salts are the most widely used, e.g., aluminum sulfate, sodium aluminate, ferrous sulfate, ferric sulfate, ferric chloride, etc. (Powell, 1954).

A large amount of work on the effect of various factors on the coagulation process in water treatment has been published and is reviewed by Packham (1962a,b). One of the important results of several works (Peterson and Bartow, 1928; Miller, 1924; Buswell and Edwards, 1922; Black et al., 1933; Marion and Thomas, 1946) is that the effectiveness of a given coagulant occurs over a limited pH range.

One of the difficulties of the above-mentioned coagulation process is that anions of the coagulant materials are introduced as contaminants. In order to avoid this, Okamoto et al. (1950) studied the use of dc or ac electrolysis with aluminum electrodes to prepare aluminum hydroxide sol for the removal of SiO_2 from underground water. The silica content was reduced from 45 ppm to 1.5 ppm with an electric power consumption of 60 kW to treat 5 tons of water/h. It was also found that pH control and violent agitation were necessary for effective operation. A similar study (Okamoto and Morozumi, 1953a) using iron electrodes instead of aluminum gave similar results for the SiO_2 variation.

In further studies (Okamoto and Morozumi, 1953b, Okamoto et al., 1956) it was found that a rise in the electrolytic resistance occurred during the electrolysis, which could be controlled by the addition of electrolytes and agitation, and that this rise was caused by scale formation on the cathode.

A recent study (El-Nokaly et al., 1985) showed that using a bimetallic, platinum–aluminum, galvanic cell without externally applied voltage reduced the silica content in simulated seawater by 93% (from 100 ppm to 7 ppm) in about 5 min. The process also had the advantage over adding aluminum salts directly in that the aluminum/silicate ratio was much lower.

These previous studies (Okamoto et al., 1950; Okamoto and Morozumi, 1953a; Okamoto and Morozumi, 1953b; Okamoto et al., 1956; El-Nokaly et al.) and the present one depend on the corrosion of the aluminum electrode to introduce aluminum ions into the solution. These alu-

0196-4321/85/1224-0468$01.50/0

minum ions in the form of $Al(OH)_3$ precipitate and cause the coprecipitation of the silica. Discussion of the details of how the aluminum is removed from the electrode and the mechanisms of the precipitation are given elsewhere (El-Nokaly et al., 1985). The necessity for the presence of NaCl was demonstrated (El-Nokaly et al.) in that in an experiment in which it was purposefully omitted from the simulated seawater no precipitation occurred even after 60 min and under identical conditions in its presence a white flocculate was observed immediately. This is due to the ability of the chloride ion to penetrate and disrupt the oxide film formed on the aluminum electrode (Edeleanu and Evans, 1951; Foley, 1970) and bring on further corrosion of the aluminum.

Another observation from the batch system study (El-Nokaly et al.) which is of importance to the present study is that short-circuiting of the cell by an external wire connecting the platinum and aluminum electrodes was necessary for precipitation to occur. This corresponds to the direct contacting of the two metals in the present multi-short-circuited galvanic cell (MSCGC) configuration and this aspect is discussed in further detail below. The use of an external power supply (6.2 V and 1.2 A) lowered the silica content in the filtrate of the batch cell from 100 ppm to 3.5 ppm in approximately the same time as for the galvanic cell to lower the silica content from 100 ppm to 7 ppm, a slight improvement.

In this paper, an attempt was made to extend the principle of coagulation by a short-circuited galvanic cell to in situ dynamic systems which can effectively remove colloidal particles with minimum cost. As a first step, we applied the static cell reported in the paper of El-Nokaly et al. in a flow system and then developed the multi-short-circuited galvanic cell (MSCGC). The effects of flow rate, nature of the aluminum surface, area of the platinum electrode, and the dissolved oxygen content of the simulated seawater solution upon the rate of colloidal silica removal using the MSCGC are discussed.

Experimental Section

The seawater simulation used was a 3.5% by weight sodium chloride aqueous solution to which 100 ppm of colloidal silica (Ludox HS-30, E. I. du Pont de Nemours & Co., Inc., Wilmington, DE) had been added.

The pretreatment system, shown in Figure 1, consists of a glass tube, the main body of which is 15 cm in length and has an i.d. of 25 mm. The inlet and outlet to the cell have inner diameters of 5.0 mm. Two different electrode configurations were investigated.

(1) Conventional Galvanic Cell. An aluminum cylinder (purified foil, J. T. Baker Co., Phillipsburg, NJ) was inserted into the glass tube and a smaller diameter platinum cylinder was inserted inside the aluminum cylinder. Platinum wires were used to assure electrical contact between the two metals.

(2) Multi-Short-Circuited Galvanic Cell (MSCGC). A platinum cylinder was inserted into the glass tube, and this cylinder was packed with aluminum foil which had been cut into narrow strips.

In the second electrode configuration (MSCGC), it was found that the way in which the aluminum strips were packed into the platinum cylinder had a significant effect on the rate of silica removal from the solution. The more contacts between the aluminum and platinum, the better the rate of silica removal and the lower the final silica content of the solution. The packing was done by loosely rolling the aluminum strips together between the palms of the hands while wearing plastic gloves and then inserting the rolled, tangled mass into the platinum cylinder. The strips were not rooled extremely tight so as to leave a loose, open, somewhat flexible network. Extreme and elaborate measures to ensure identical packing from run to run were not taken as this would defeat the purpose of simplicity of the cell and operation and also the cell could be readily designed so that when contact between the aluminum strips and the platinum was broken due to corrosion, it could be reestablished by the solution flow. All the results presented, except for those dealing with variation of the platinum electrode size, employ a platinum electrode with an area of 25.0 cm^2 and an aluminum area of 56.25 cm^2 (either left as a sheet or cut into strips).

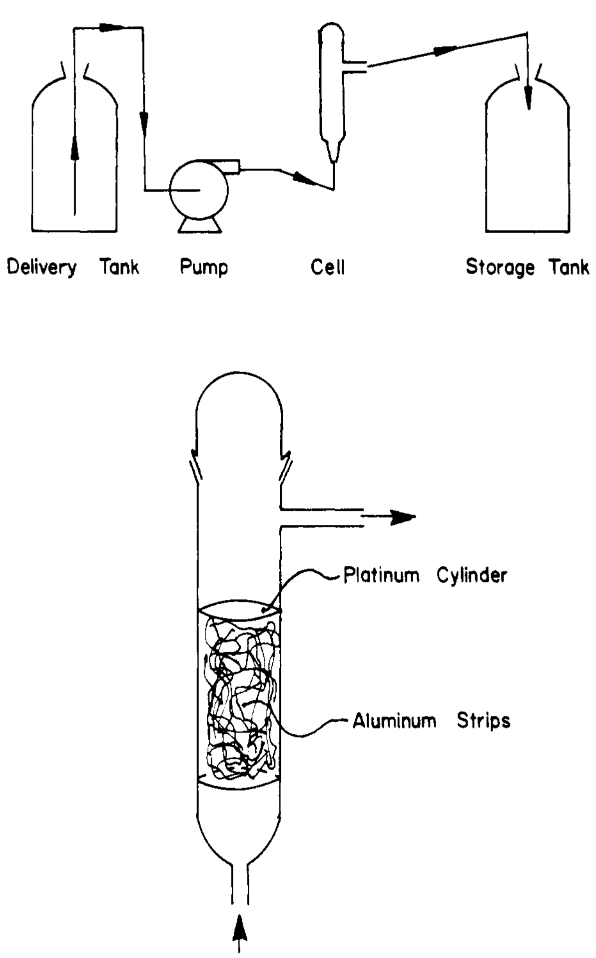

Figure 1. Schematic of pretreatment system and detail of flow configuration of multi-short-circuited galvanic cell (MSCGC).

The galvanic cell was connected to a sealless magnetic drive centrifugal pump, with variable flow control, by means of Tygon tubing. Three liters of the simulated seawater solution was pumped through the cell and collected in a storage bottle. The bottles were interchanged and the procedure was repeated. The same solution was pumped through the cell 10 to 20 times. Samples were collected after various cycles and the filtrate was analyzed for oxygen, silica, and aluminum contents. After an experiment the platinum electrode was cleaned ultrasonically in deionized water and the corroded aluminum strips or sheet were discarded, except in the experiment dealing with the effect of the condition of the aluminum surface.

A. Analysis. 1. Silica. The silica content was determined by the method of reaction of orthosilicic acid (H_4SiO_4) with molybdate to form the yellow silicomolybdic acid after the colloidal silica had been depolymerized in order to react completely with molybdic acid (Iler, 1979). The absorbance of the yellow solution was measured at 410 nm (visible). The silica reacted fully in approximately 2 min and gave a maximum absorption value. These maximum values were used to calculate the results reported in this paper.

2. **Aluminum.** The aluminum content of the filtrates was determined by complexometric titration with Eriochrome Black T as the indicator (Vogel, 1961).

3. **Dissolved Oxygen Content.** The amount of dissolved oxygen (ppm) contained by the solutions was determined with an Orion Research Model 97-08 oxygen electrode connected to an Orion 901 microprocessor. After every third cycle during an experimental run, approximately 50 mL of solution was placed in a sample tube. The oxygen electrode was then inserted in the tube and the oxygen content was recorded after the reading had stabilized, normally 2 to 5 min after insertion of the oxygen electrode.

Results and Discussion

Earlier studies have shown that colloidal silica in seawater is effectively removed down to approximately 7 ppm by using a bimetallic (Pt–Al) galvanic cell without an external power source (El-Nokaly et al.).

In this study, we have used a dynamic cell configuration as shown in Figure 1. The effect of the flow rate of solution through the galvanic cell and the effect of variation of the area of the platinum electrode as well as the effect of the surface condition of the aluminum electrode and the dissolved oxygen content of the solution have been investigated.

All of the results presented in this paper are for the filtrate after the precipitate had been removed by centrifuging. The results on silica content of the solutions are reported as the ratio of the absorbance of the sample solution, A, to the absorbance of the initial (100 ppm silica) solution, A_0. Since the intensity of the absorption changes with time, standards would need to be run with each run of samples in order to calculate the silica content of each solution from its absorbance value. However, the correlation between absorbance and silica content is linear, and therefore the ratio of A/A_0 will remain constant for a given silica concentration, no matter what the actual values of the absorbances.

The time scale of the experiments is reported as contact time which is the time a volume of the salt solution equal to the volume occupied by the electrodes is in contact with the electrodes. This contact time is given by T in the equation

$$T = v_0/F$$

where v_0 is the electrode volume, 25.4 cm^3 in these experiments, and F is the solution flow rate in cubic centimeters per second. This gives the contact time in seconds.

Since the flow rate is maintained at a constant value within the slight variations of the pump throughout an experimental run, the value of the contact time does not vary from cycle to cycle. Even though the solution volume decreases, due to the removal of the samples for analysis, the time to pump the solution through the cell decreases proportionally.

Since the contact time is a constant throughout an experimental run, the total contact time elapsed is given by the product of contact time, T (constant for a given flow rate) and the number of cycles that have been pumped through the cell.

Figure 2 shows a plot of the relative absorbance, A/A_0, of the yellow silicomolybdic acid at 410 nm as a function of the contact time for different flow rates.

At the lower flow rates we observe initially a slow rate of silica removal for short contact times. This indicates that an induction time for corrosion to start on the aluminum surface is required. The fact that this induction period appears to be missing at the two highest flow rates can be interpreted as requiring a certain volume of solution to contact the electrodes for corrosion to start occurring appreciably and this occurs sooner as the flow rate is increased. The decrease in induction period could also be due to the increased turbulence of the flow through the cell as flow rate increases. Once the rate of corrosion of the aluminum electrode is efficient, the silica content of the seawater is rapidly reduced and reaches a steady-state value of approximately 5 ppm, i.e., a reduction of ca. 95%.

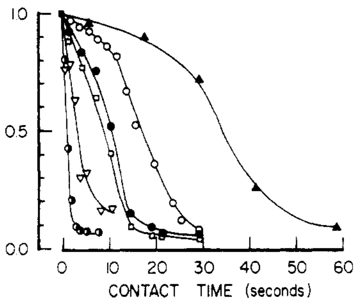

Figure 2. Change of silica content of the filtrate with contact time, at various solution flow rates. (Area of Pt electrode = 25.0 cm^2; area of Al electrode = 56.25 cm^2; conventional galvanic cell, solution flow rates: (▲) 0.25 L/min; (○) 0.75 L/min; (●) 1.0 L/min; multi-short-circuited galvanic cell, solution flow rates: (□) 1.0 L/min; (▽) 2.7 L/min; (◑) 3.8 L/min.)

The conventional galvanic cell data come from a direct extension of the static, batch galvanic cell configuration (El-Nokaly et al.) to a flow system. The major difference between the static cell and the conventional galvanic cell of this study is that the external connection of the static system is immersed in the flow of our dynamic system. This creates a short circuit, and it was observed that the majority of the aluminum corrosion occurred near the connection between the platinum wire and the aluminum electrode, as evidenced by greater pitting and more holes in the aluminum near the connection. Due to this observation, it was decided to use the second electrode configuration (MSCGC) with the aluminum cut into strips and packed into the platinum cylinder. This configuration would allow for more contact points between the aluminum and the platinum and, therefore, faster corrosion of the aluminum causing faster precipitation of the aluminum and with this faster coprecipitation of the colloidal silica. Two other effects of the MSCGC are that the packing increases the turbulence of the flow which causes better contacting of the solution with the electrodes and also could help to disturb formation of a passivating oxide layer on the aluminum. Also, the strips are more mobile than a single aluminum sheet so that loss of contact between the aluminum and the platinum caused by corrosion of the aluminum could be reestablished by movement of the aluminum strips due to the flow.

The aluminum content of the solution increases with contact time as expected and the content is higher at the higher flow rates. Also, the content appears to reach a saturation value as contact time increases. Typical curves of aluminum content vs. contact time are shown in Figure 3, and are similar to the results of El-Nokaly et al. for the batch cell.

In a separate set of experiments the effect of the state of the aluminum electrode surface was investigated. A clean platinum electrode and new aluminum strips were placed in the cell and a fresh solution was pumped through 10 times. As seen in Figure 4, the data for this run are almost identical with a typical 20-cycle run *starting* with

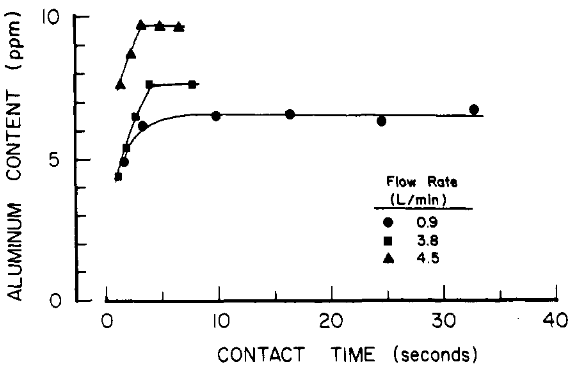

Figure 3. Change of aluminum content of the filtrate with contact time, at various solution flow rates (electrode areas same as in Figure 2, MSCGC).

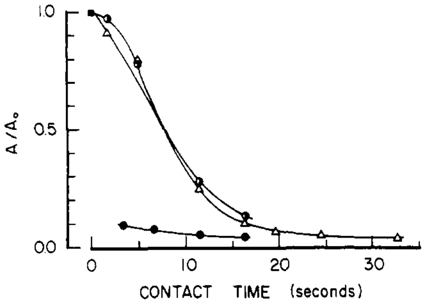

Figure 4. Effect of condition of aluminum electrode on silica content of the filtrate, at a solution flow rate of 0.9 L/min (electrode areas same as in Figure 2, MSCGC): (△) 20 cycles starting with 100 ppm SiO_2 solution and clean electrodes; (◑) 10 cycles starting with 100 ppm SiO_2 solution and clean electrodes; (●) 10 cycles starting with 100 ppm SiO_2 solution, but using the same electrodes as in (◑) experiment; i.e., precorroded, uncleaned electrodes).

clean electrodes and 100 ppm SiO_2 solution. However, after the 10-cycle run, the electrodes were left in the cell and a new 100 ppm SiO_2 solution was pumped through 10 times. That is, the aluminum electrode was already corroded and, as can be seen in Figure 4, the induction time is effectively removed and the silica content decreases by more than 90% in ~3 s. If the electrodes were rinsed in deionized water, prior to running the second fresh base solution through the cell, the curve obtained would be the same as those obtained starting with new clean electrodes (upper curves of Figure 4).

In an earlier study (El-Nokaly et al.), it was found that the size of the aluminum electrode did not affect the rate of silica removal from seawater. Mansfeld and Kenkel (1976) found that the galvanic cell current is independent of the area of the anode (the Al electrode in this case) but directly proportional to the area of the cathode (the Pt electrode).

In order to study the effect of the Pt-electrode surface area upon the rate of silica removal, we ran identical base solutions through the cell with a Pt-electrode surface area of 10, 25, and 100 cm^2, respectively. As can be seen from Figure 5, the size of the Pt-electrode surface area does affect the rate of silica removal from seawater in the MSCGC configuration. The larger Pt-surface area electrode reduces the silica content faster than do the smaller ones.

Figure 6 shows that the silica removed from the solution at a given contact time is directly proportional to the surface area of the Pt electrode, as Mansfeld found for the galvanic current. The more important results of increasing the platinum electrode size, in this flow MSCGC configuration, is that it increases the number of aluminum to platinum contact points. For all the experiments it was observed that the most severe pitting or corrosion occurred at the points of contact between the two metals, with less pitting on the aluminum in the center of the cell (i.e., not in direct contact with the platinum). Therefore, the rate of aluminum ion introduced to the solution or efficiency of the cell for colloidal silica removal is increased by increasing the number of contact points. At the longer contact times in Figure 6 the direct proportionality does not hold because for the cell in which a 100-cm^2 Pt electrode was employed the silica content has already reached or almost reached its final level and can no longer be lowered.

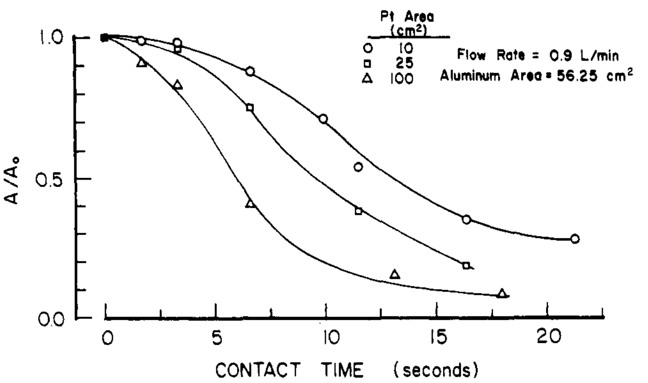

Figure 5. Effect of size of platinum electrode on silica content of the filtrate vs. contact time (MSCGC).

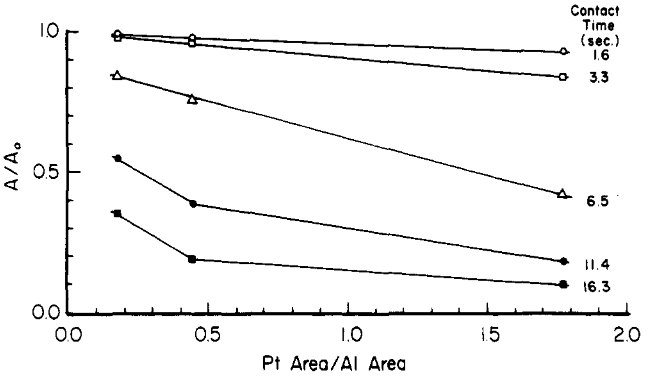

Figure 6. Silica content of the filtrate vs. ratio of platinum electrode area to aluminum electrode area, at various contact times (MSCGC, solution flow rate = 0.9 L/min; aluminum electrode area = 56.25 cm^2).

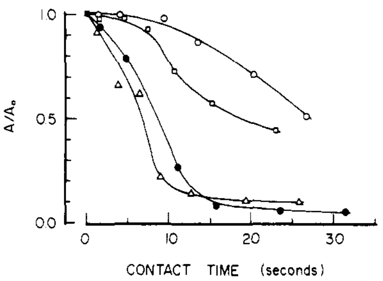

Figure 7. Effect of gas addition to storage tank, to change the dissolved oxygen content of the solution, on the silica content vs. contact time curves (electrode areas as in Figure 2, MSCGC; average dissolved oxygen content of solutions: (●) 5.2 ppm, no gas added; (△) 5.2 ppm, air added; (□) 1.5 ppm, argon added; (○) 1.3 ppm, nitrogen added).

Addition of gases to either enrich or deplete the dissolved oxygen content of the solutions was accomplished by bubbling the gas (air, nitrogen, or argon) into the delivery tank at a set flow rate until the oxygen content attained a stable level, prior to the start of the run. The gas was then bubbled at that rate in the storage tank throughout the cycling of the tanks.

Figure 7 shows the relative absorbance vs. contact time for this series of experiments. The solution flow rate through the cell was maintained at about 1.0 L/min in all cases. The sizes of the electrodes used were Pt, 25 cm^2 and Al, 56.25 cm^2, with the aluminum electrode cut into strips and inserted in the platinum cylinder, as described earlier (MSCGC).

The addition of argon and nitrogen, at flow rates of 1.0 and 1.1 L/min, respectively, decreased the average amount of dissolved oxygen in the solution from 5.2 ppm, for a solution with no gas added, to 1.5 ppm and 1.3 ppm, respectively. These decreases in oxygen level decreased the rate of silica removal due to decreased corrosion of the aluminum electrode.

The addition of air, at a flow rate of 1.0 L/min, did not significant change the oxygen level of the solution, lowering it to 5.16 ppm from 5.24 ppm. Similarly, the rate of silica removal for the air addition case is nearly the same as that for the case where no gas was added.

Consideration of the electrochemistry of the aluminum/platinum galvanic system gives an explanation for the effect of dissolved oxygen content on the colloidal silica removal. Dissolved oxygen affects the reaction at the cathode (platinum) according to

$$^3/_4O_2 + {}^3/_2H_2O + 3e^- \rightarrow 3OH^-$$

influencing the rate of formation of OH$^-$ which is needed to form $Al(OH)_3$, the coagulating agent, at the anode surface. This explains the observed decrease in the rate of colloidal silica removal when the dissolved oxygen content of the solution was lowered (by addition of argon or nitrogen), due to the decrease in $Al(OH)_3$.

Another place where dissolved oxygen enters the corrosion process is in the formation of aluminum oxide on the anode surface, in the conventional galvanic cell of aluminum/platinum

$$2Al(OH)_3 + O_2 \rightarrow Al_2O_3{\cdot}nH_2O$$

The formation of the aluminum oxide layer passivates the aluminum anode surface and retards further corrosion. However, in solutions containing chloride ions, the chloride ions are attracted to the electrode, penetrate the oxide layer, and disrupt formation of the oxide film (Edeleanu and Evans, 1951; Foley, 1970). Soluble cations are formed from the aluminum hydrate chloride complexes (El-Nokaly et al.).

Another area in which the galvanic and MSCGC configurations are advantageous is in bringing the colloidal silica together with the aluminum ions to be precipitated. For the conventional treatment method of adding aluminum salts to the solution, the colloidal silica and aluminum ions are brought together by diffusion and relatively weak intermolecular electrostatic forces between the positively charged aluminum ions and the negatively charged silica. In this case mixing would be vital for effective precipitation.

In the conventional galvanic cell, there is the advantage that the silica particles are attracted to the anode due to the electric field, the force of which extends far beyond the range of other intermolecular forces (i.e., the electrostatic or coulombic forces between aluminum ions and silica particles). Since the aluminum ions are being produced at the anode and the silica particles are being drawn to the anode, a greater efficiency of coprecipitation would be expected in the galvanic cell over that achieved by addition of aluminum salts.

However, in conventional galvanic cells, if the products of the electrochemical reactions occurring at the electrodes are formed faster than they can be removed (by precipitation), then concentration polarization occurs. Efficient stirring is required to prevent concentration polarization and the associated decreases in current and dissolution of the electrode material (Packham, 1963; El-Nokaly et al.). Even though rapid stirring will increase the current and, therefore, the metal dissolution rate, careful control of the stirring is necessary since too rapid stirring will break up coagulated particles (Healy et al., 1973; Iler, 1973).

On the other hand, the fact that the flow passes through the aluminum strips in the MSCGC configuration forces the colloidal silica particles and the chloride ions into close contact with the aluminum (anode) and, therefore, the aluminum ions, additional stirring to increase the diffusion of the colloidal silica particles or chloride ions is not necessary. Moreover, the turbulence or mixing created by the flow is sufficient to prevent concentration polarization and to aid in the prevention of formation of a passivating oxide layer.

At least in the range of flow rates examined, the turbulence caused by the flow through the packed aluminum strips was not too great as to prevent agglomeration of the precipitating colloids. However, this is only a problem when the solution is cycled through the MSCGC cell several times. If only one pass through the MSCGC cell were employed, the problem of turbulence breaking up the agglomerating particles would be avoided as agglomeration occurs downstream from the MSCGC cell where the dissolution is occurring. In contrast, the dissolution and the precipitation are occurring in the same vessel in the conventional galvanic cell process and careful control of stirring is required, as mentioned previously.

Conclusions

In conclusion, we have shown that a dynamic, MSCGC can be an important and above all inexpensive device to use to remove colloidal silica in the pretreatment of seawater or brackish water which contains a considerable amount of colloidal silica.

The rate of silica removal is enhanced by higher solution flow rates through the cell, a greater number of contacts between the platinum and aluminum, and is greatly enhanced by use of a precorroded aluminum electrode (uncleaned). The rate is detrimentally affected by lowering the dissolved oxygen content in the solution, but the amount normally dissolved in the simulated seawater (i.e., $\sim$5.2 ppm O_2) is sufficient for efficient operation of the cell.

The design of the cell should be such that the number of points of contact between the aluminum and the platinum is maximized and the flow pattern through the cell is such that as the contact points are broken by consumption of the aluminum they are reestablished by the flow. The system should lend itself very easily to a modular form since the platinum is not consumed and could form the body of a module which when the aluminum is entirely consumed would simply be removed and repacked with fresh aluminum. The module could be placed in present water pretreatment systems since the flocculation increases the size of the colloidal material to a size which can be easily removed by conventional filtration or sedimentation systems prior to the reverse osmosis membrane system.

Registry No. Pt, 7440-06-4; Al, 7429-90-5; SiO_2, 7631-86-9; O_2, 7782-44-7.

Literature Cited

Armstrong, F. A. J. In "Chemical Oceanography"; Riley, J. P.; Skirrow, G., Ed.; Academic Press: London, 1965; Vol. I, p 409.
Black, A. P.; Rice, O.; Bartow, E. *Ind. Eng. Chem.* **1933**, *25*, 811.
Buswell, A. M.; Edwards, G. P. *Chem. Metal. Eng.* **1922**, *26*, 826.

Ind. Eng. Chem. Prod. Res. Dev. **1985**, *24*, 473–478

Edeleanu, C.; Evans, V. R. *Trans. Faraday Soc.* **1951**, *47*, 1121.
El-Nokaly, M. A.; Huseuh-Ler, L.; Friberg, S. E.; Yasuda, H. K. *J. Disp. Sci. Tech.* **1985**, in press.
Foley, R. T. *Corrosion* **1970**, *26*, 58.
Healy, T. W.; Wiese, G. R.; Yates, D. W.; Kavanaugh, B. V. *J. Colloid Interface Sci.* **1973**, *42*, 647.
Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979; p 97.
Iler, R. K. *J. Colloid Interface Sci.* **1973**, *43*, 399.
Liss, P. S. In "Chemical Oceanography"; Riley, J. P.; Skirrow, G., Ed.; Academic Press: London, 1975; Vol. II, p 193.
Mansfeld, F.; Kenkel, J. V. In "Galvanic Pitting and Corrosion-Field and Laboratory Studies", ASTM STP576; American Society for Testing and Materials: Philadelphia, 1976; p 20.
Marion, S. P.; Thomas, A. W. *J. Colloid Sci.* **1946**, *1*, 21.
Miller, L. B. *U.S. Pub. Health Service, Pub. Health Report* **1924**, *39*, 1502.
Okamoto, G.; Morozumi, T. *J. Electrochem. Soc. Jpn.* **1953a**, *21*, 512.
Okamoto, G.; Morozumi, T. *J. Electrochem. Soc. Jpn.* **1953b**, *21*, 573.
Okamoto, G.; Morozumi, T.; Sato, N.; Hachiya, M.; Nagayama, M. *J. Electrochem. Soc. Jpn.* **1956**, *24*, 269.
Okamoto, G.; Okura, T.; Sudo, N. *J. Electrochem. Soc. Jpn.* **1950**, *19*, 289.
Packham, R. F. *Proc. Soc. Water Treat. Exam.* **1962a**, *11*, 50.
Packham, R. F. *Proc. Soc. Water Treat. Exam.* **1962b**, *11*, 602.
Packham, R. F. *Proc. Soc. Water Treat. Exam.* **1963**, *12*, 15.
Peterson, B. H.; Bartow, E. *Ind. Eng. Chem.* **1928**, *20*, 51.
Powell, S. T. "Water Conditioning for Industry"; McGraw-Hill: New York, 1954; Chapter 3.
Vogel, A. I. "A Textbook of Quantitative Inorganic Analysis"; Wiley: New York, 1961; pp 425–436.

Received for review November 1, 1984
Accepted March 8, 1985

Solubility, Solvency, and Solubility Parameters

John W. Van Dyk,* Harry L. Frisch,† and Dao T. Wu

Marshall R&D Laboratory, E. I. du Pont de Nemours and Co., Inc., Philadelphia, Pennsylvania 19146

Three-component solubility parameter envelopes have been useful in predicting the solubility/nonsolubility of polymers. The use of three-component solubility parameters in predicting both degree of solvency (as measured by inherent viscosity) and solubility/nonsolubility is demonstrated. Predictability is significantly worse if the total solubility parameter is substituted for the three-component parameters. Predictability is significantly improved if the effect of solvent molar volume on solubility is included. These conclusions are based on data for the solubility of three methacrylate polymers in 34 potential solvents. Inherent viscosity data for each of the polymers (for those solvents in which they are soluble) are also given. Three equations (two of which are based on available theory) are used to correlate inherent viscosity with solubility parameter.

Introduction

In spite of its many theoretical limitations (Burrell, 1968; Nelson et al., 1970) the three-component solubility parameter approach has been very useful in dealing with problems of polymer solubility. Although many other approaches (Drago et al., 1977; Flory, 1953a; Fowkes and Mostafa, 1978; Gutman, 1977; Huggins, 1972) have been suggested, the use of solubility parameters is, at the moment, the *only* practical way of predicting polymer solubility. Unlike other approaches, solubility parameters give the ability to predict the solubility of a polymer in a mixture of solvents from two sets of parameters, where one set is specific to individual pure solvents and independent of the polymer and the other set is specific to the polymer and independent of the solvent mixture.

Although other systems (Crowley et al., 1966; Nelson et al., 1970) are available, we chose Hansen's three-component solubility approach (Hansen, 1967a) because (1) reliable "experimental" values are available for many solvents (Hansen and Beerbower, 1971), (2) reliable methods are available for calculating values of solvents having no experimental values (Hansen, 1967a,c; Hoy, 1970; Rheineck and Lin, 1968; Van Krevelen and Hoftyzer, 1976), and (3) the solubility envelope of many polymers can be represented by a sphere in Hansen solubility space if the nonpolar parameter is suitably scaled (Hansen, 1967b).

The usual method of determining the solubility envelope of a polymer involves measuring the solubility of a polymer (at a fixed concentration) in a series of solvents having known solubility parameters.

From the positions of the solvents in solubility space and from a knowledge of those solvents in which the polymer is soluble, an envelope in solubility space, which surrounds the soluble region, is deduced. The location of this envelope is determined by the change from soluble to insoluble. Within the envelope most of the solvents will dissolve the polymer; outside the envelope most of the solvents will not dissolve the polymer. If the solubility region is spherical, it can be represented by four parameters—the three solubility parameters corresponding to the center of the sphere and the sphere radius. It should be noted that this approach locates the center of the sphere on the basis of the location of its boundaries. All solvents are given the same weight. Good solvents are not differentiated from poor solvents.

In this paper we have subjected the three-component solubility parameter approach to a more critical test by assessing its ability to predict both degree of solvency [via inherent viscosity (Ahmad and Yaseen, 1978; Bristow and Watson, 1958b; Cowie, 1968; Mangaraj et al., 1963; Sosa et al., 1977)] and solubility/nonsolubility. The solubilities of three methacrylate polymers (methyl, ethyl, and butyl) were determined by using 34 potential solvents. In addition, the inherent viscosities (at 0.5 g/dL) for all the resulting solutions (12 for PMMA and 16 for PEMA and PBMA) were measured. Three equations (two of which are based on available theory) were used to correlate the inherent viscosities and solubility/nonsolubility with three-component solubility parameters.

Theoretical Considerations

A. Solubility Parameter. The Hansen system consists of three parameters: δ_n, nonpolar; δ_p, polar; and δ_h, hydrogen bonding.

These three parameters are related to the total solubility parameter (δ_t) by the following equation.

$$\delta_t = (\delta_n^2 + \delta_p^2 + \delta_h^2)^{1/2} \tag{1}$$

---

†Suny, Albany, NY 12222.

0196-4321/85/1224-0473$01.50/0