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Use of Strong Base Organic Anion Exchangers for the Removal of Suspended Alumina Particles in Light Water/Heavy Water Systems

K. S. Venkateswarlu[a]; A. S. Gokhale[a]; G. Venkateswaran[a]
[a] WATER CHEMISTRY DIVISION, BHABHA ATOMIC RESEARCH CENTRE TROMBAY, BOMBAY, INDIA

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NOTE

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K. S. VENKATESWARLU, A. S. GOKHALE, and
G. VENKATESWARAN

WATER CHEMISTRY DIVISION
BHABHA ATOMIC RESEARCH CENTRE
TROMBAY, BOMBAY 400085, INDIA

Abstract

A method for the removal of suspended alumina particles from H_2O/D_2O systems has been developed. It is based on the modification of surface charge of the suspended hydrated alumina particles by the addition of sulfate ions and adsorbing them on conventional strong base anion exchanger. 48 ppm of added sulfate has been found to be the required concentration for treating 30 ppm $Al_2O_3 \cdot 3D_2O$ suspensions.

INTRODUCTION

The problem of turbidity generation due to suspended alumina particles in cooling water systems employing heavy water as the coolant and aluminum as the fuel clad is known to have occurred in many research reactors in the world (*1-3*). Erosion/corrosion of the heat-exchanging aluminum surface and hydrolysis of the Al^{3+} ions leading to the microcrystallization of the sparingly soluble $Al(OH)_3$ at the near-neutral pH (6.1) of the D_2O coolant have been given as the reasons for the appearance of turbidity. The normal (organic polymer based) strong acid (H^+)-strong base (OH^-) ion-exchange resins employed in reactor coolant purification have not been found to be effective in removing these colloidal particles. In addition, the sorption characteristics exhibited by these alumina particles for uranium and other radioactive fission products make the coolant purification system less efficient in controlling the buildup of such radioactive species. Because of this, in a recirculating system such as the primary coolant system of a nuclear reactor the buildup of turbidity results in problems of increasing radioactivity transport and deposition on system surfaces, thus making budgeting more difficult for operation and maintenance tasks.

Many on-line chemical methods have recently been developed and employed for the removal of turbidity from reactor systems (*2*–*4*), but these involve the development of a specific adsorber material like fibrous carbon electrodes (*2*) or an ion-exchange matrix with a built-in adsorbing material like magnesium hydroxide (*3*) or hydrous titanium oxide (*4*). On the other hand, the method described in this paper modifies the surface charge characteristics of the hydrated colloidal alumina particles in the aqueous medium and adsorb them on the conventional strong base anion-exchange resin employed in the purification system.

EXPERIMENTAL AND RESULTS

Preparation of Hydrated Alumina Suspensions

Synthetic aluminum turbidity in light water was prepared by equilibrating AR grade fine aluminum powder (which was activated chemically by washing with 1:1 HCl and subsequently made free of chloride by washing with demineralized water) with demineralized water at about 340 K for 4 to 5 h with constant brisk stirring and then filtering through a 4.8-μm pore size filter paper. Freshly prepared turbidity showed particles larger than 0.2 but smaller than 1.1 μm in size, while the 3 day-old turbidity showed 40% of the particles larger than 1.1 μm but smaller than 4.8 μm. The pH of the different lots of turbidity prepared was in the region 6.1 ± 0.1. Turbidity was measured by the nephelometric method with reference to a standard suspension of silica. In addition, percentage transmission at 390 nm observed as referenced to transmission given by demineralized water was also used as a measure of the turbidity of the solution. The ratio of turbidity value of the alumina suspension as measured against silica scale to its Al cocnentration was found to be about 15. X-ray diffraction analysis of these particles gave peaks corresponding to *d*-spacings of 4.720, 4.367, 3.192, 2.216, and 1.712 Å, which showed the crystal modification of these suspended particles as γ-$Al(OH)_3$ or bayerite. The negative charge on thse particles was identified by electrophoretic mobility measurements at pH 6.1 which was expected from the reported point-of-zero charge (pzc) value of 5.4 (*5*) for bayerite. Thus the laboratory-generated turbidity resembled the reactor-system generated turbidity (*3*) which was identified as bayerite aging to gibbsite [α-$Al(OD)_3$ or α-$Al_2O_3 \cdot 3D_2O$].

Ion-Exchange Resins

20–50 mesh (U.S.) strong base-type anion exchanger (in OH^- form) was used in all the experiments either individually or in combination with 20–50 mesh strong acid-type cation exchanger (in H^+ form).

Addition of Sulfate Ions to the Turbidity Solutions

Calculated quantities of AR potassium sulfate were added to the hydrated alumina suspensions to give different sulfate ion concentrations except in one case where H_2SO_4 was added.

Tables 1 and 2 show the influence of sulfate ion addition on turbidity clearance by the conventional anion exchanger. It is clear that a minimum concentration of ~50 ppm of SO_4^{2-} ion is required if the OH^- form of anion exchanger has to pick up the colloidal particles of hydrated alumina. On the other hand, anion exchanger taken in the sulfate form

TABLE 1
Influence of the Addition of Sulfuric Acid on Aluminum Turbidity (laboratory generated) Removal[a]

Sample description	Al^{3+} (ppm)	pH	% Transmittance	Turbidity on silica scale (ppm)
Before passing through the anion exchanger	25	3.0	40	375
After passing through the anion exchanger	0.1	8.0	99	<2

[a] Adsorber: 20–50 mesh OH^- form of anion exchanger. Adsorber bed volume: 1 mL. (SO_4^{2-}) as H_2SO_4: 48 ppm. Volume of turbid solution passed: 10 mL.

TABLE 2
Influence of the Addition of K_2SO_4 on the Removal of Aluminum Turbidity[a]

Parameter	Value of turbidity parameters measured with varying amounts of sulfate as K_2SO_4 added to the turbid solution before and after passing through anion exchanger		
	25 ppm SO_4^{2-}	50 ppm SO_4^{2-} [b]	100 ppm SO_4^{2-}
Al^{3+}	25/25	25/0.1	25/0.1
pH	6.0/6.0	6.0/10	6.0/10
% Transmittance	40/40	40/99	40/99
Turbidity on silica scale (ppm)	375/375	375/<2	375/<2

[a] Adsorber: 20–50 mesh OH^- form of anion exchanger. Adsorber bed volume: 1 mL. Volume of turbid solution passed: 10 mL.

[b] >400 mL of 375 ppm turbid solution into which 50 ppm of SO_4^{2-} has been added could be cleared by passing through a 6-mL bed volume resin, thereby realizing a capacity of >2.5*E* + 04 ppm-bed volumes.

and not in the OH^- form was found to be ineffective in removing the turbidity from solutions to which no sulfate had been added.

Table 3 shows the capacity of the OH^- form of an anion exchanger in removing Al turbidity from solutions to which SO_4^{2-} has been added but with the additional feature of incorporating a cation bed below the anion bed [the two types of resins being separated by a thin layer (~2 mm thickness) of quartz wool] to recover the turbidity-free water at proper pH and specific conductivity values. Another difference in the results presented in Table 3 and those in Table 2 is the initial turbidity value of the solution treated. It is seen that irrespective of the initial turbidity value, the anion exchanger shows similar turbidity removal capacities (as expressed in ppm-bed volumes).

Table 4 shows the results obtained with reactor-generated turbidity in D_2O. Turbidity removal capacity similar to that achieved with laboratory-generated turbidity could be realized. The slight pH decrease observed after passing through the anion–cation resin series could be due to some other cationic species like Mg^{2+} present in the reactor coolant exchanging with the H^+ in the cation bed.

DISCUSSION

With a pzc of 5.4 in a medium of pH 6.1 in the presence of H^+ and OH^- as the only potential-determining ions, the bayerite/gibbsite particles are negatively charged according to

TABLE 3
Turbidity Removal by Sulfate Addition and Recovery of Original Turbidity-Free Demineralized Water[a]

Sample description	% Transmittance	Turbidity on silica scale (ppm)	pH	Specific conductivity (μS/cm)
Before passing through the adsorber but after adding K_2SO_4	77	37	6.0	125
After passing through the adsorber	99	<2	6.0	2.0

[a] Adsorber: 20–50 mesh OH^- form of anion exchanger backed up by 20–50 mesh H^+ form of cation exchanger. Bed volume: 11.5 mL anion exchanger backed up by 11.5 mL cation exchanger. Flow rate: 11.5 mL/m. SO_4^{2-} = 48 ppm. Volume of turbid solution passed = 4.5 L. Ppm-bed volumes realized with respect to volume of anion exchanger (adsorber) only: >1.5*E* + 04.

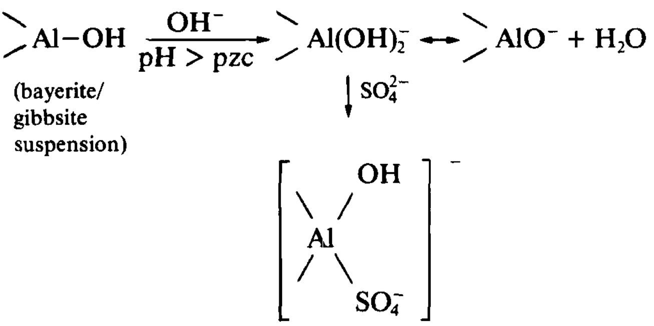
TABLE 4
Removal of Reactor-Generated Turbidity from Heavy Water[a].

Sample description	Turbidity on silica scale (ppm)	pH
Before passing through the adsorber but after adding K_2SO_4	158	6.6
After passing through the adsorber	<2	6.2

[a] Adsorber: 20–50 mesh OH^- form of anion exchanger backed up by 20–50 mesh H^+ form of cation exchanger. Bed volume: 3 mL anion exchanger backed up by 3 mL cation exchanger. Flow rate: 3 mL/m. SO_4^{2-} = 48 ppm. Volume of turbid solution cleared: 290 mL. Ppm-bed volumes cleared with respect to volume of anion exchanger (adsorber) only: >1.6*E* + 04.

$$\zeta = k(\text{pzc} - \text{pH})$$

where ζ is the zeta potential which is a measure of the surface charge of the particles and k is a proportionality constant. Sulfate ions when added could be specifically adsorbed on the hydrated alumina particles:



Modi and Fuerstenau (*6*) pointed out that at a concentration of 29 ppm (*3E-04M*) of added SO_4^{2-} ions, the positively charged corundum (α-Al_2O_3) undergoes a reversal in surface charge. The pzc of corundum (9.45) undergoes an acidic shift by 2.9 pH units in the presence of added sulfate. The surface-active ions act not only by simple electrostatic forces but also by strong chemical or covalent forces. Letterman and Vanderbrook (*7*) observed that a concentration of >1920 ppm of added sulfate is required to restabilize the aluminum-hydroxide-coated kaolin particles by making them negatively charged at all aluminum concentrations. At SO_4^{2-} less than 1920 ppm but greater than 290 ppm, restabilization does not occur even at high Al concentration.

In the present study, sulfate ions at >48 ppm concentration was found to make the hydrated alumina particles sufficiently negatively charged to make the OH^- ions in the anion exchanger labile and to become adsorbed on the positively charged anion substrate.

Since the resin particle employed in this study conforms to the standard bead size of the ion-exchangers used in the reactor coolant purification system, one can realize (at least in the initial stages of column operation) high flow rates without encountering significant pressure drop problems, thereby achieving shorter cleanup half lives.

COMPARISON OF THE TURBIDITY REMOVAL CAPACITY OF THE PRESENT METHOD WITH THAT OF SOME OTHER METHODS STUDIED EARLIER

The turbidity removal capacity of the present sulfate ion addition method seems to be limited by the exchange capacity of the strong anion exchanger taken. Therefore, based on an exchange capacity value of 1.2 meq/mL of the strong anion exchanger used in this study and at a concentration of 48 ppm of added sulfate, a maximum turbidity removal capacity of 5*E* + 04 ppm-bed volumes is possible. Hence, sulfate ion addition in excess of the minimum required concentration for turbidity removal (namely 48 ppm) results in the rapid exhaustion of the anion exchanger and hence interferes with the turbidity removal capacity of the anion exchanger. For an alumina turbidity where the suspended hydrated alumina ($Al_2O_3 \cdot 3D_2O$) absolute concentration is 30 ppm (or 150 ppm turbidity on the silica scale), 1 kg of the anion exchanger can clear turbidity from 0.4 m^3 of the suspension. This can be compared with the following turbidity removal capacities reported in earlier studies: 1 kg of fibrous carbon electrodes treating 5 m^3 of 6 ppm $Al_2O_3 \cdot 3D_2O$ suspension (*2*) (i.e., 1 m^3 of 30 ppm $Al_2O_3 \cdot 3D_2O$) or 1 kg of magnesium hydroxide precipitated resin treating 2.5 m^3 of a 30 ppm $Al_2O_3 \cdot 3D_2O$ suspension (*3*).

CONCLUSION

A method has been developed for removing alumina turbidity from light water/heavy water systems. The method is based on modification of the surface charge of the suspended hydrated alumina particles by the addition of sulfte ion and having them adsorbed onto the normal anion exchanger used in reactor coolant purification circuits. 48 ppm of sulfate ions has been found to be the optimum concentration required for this purpose. By having a backup cation exchanger, the outlet water could be ensured of having its required demineralized quality when it is returned to the reactor main system.

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REFERENCES

1. S. R. Hatcher and H. K. Rae, "Formation and Control of Turbidity in Aluminum-Water Reactor Systems," *Nucl. Sci. Eng., 10,* 316 (1961).
2. H. Tobias, E. Taragan, Y. Oren, and A. Soffer, "Removal of Suspended Alumina Particles from Heavy Water by Electroadsorption on Fibrous Carbon Electrodes," *Nucl. Technol., 77,* 46 (1987).
3. K. S. Venkateswarlu, R. Shanker, S. Velmurugan, G. Venkateswaran, and M. R. Rao, "Removal of Aluminum Turbidity from Reactor Heavy Water by Precipitation Ion-Exchange Using Magnesium Hydroxide," *Ibid., 82*(9), 243 (1988).
4. B. Venkataramani, S. B. Karweer, R. K. Iyer, G. M. Phatak, and R. M. Iyer, "Removal of Al(III)-Based Turbidity in Water Using Hydrous Titanium Oxide Dispersed in Ion-Exchange Resins," *Sep. Sci. Technol., 23,* 473 (1988).
5. G. A. Parks, "The Iso-Electric Points of Solid Oxides, Solid Hydroxides and Aqueous Hydroxo Complex Systems," *Chem. Rev., 65,* 177 (1965).
6. H. J. Modi and D. W. Fuerstenau, "Streaming Potential Studies on Corundum in Aqueous Solutions of Inorganic Electrolytes," *J. Phys. Chem., 61,* 640 (1957).
7. R. D. Letterman and S. G. Vanderbrook, "Effect of Solution Chemistry on Coagulation with Hydrolyzed Al(III)—Significance of Sulfate Ion and pH," *Water Res., 17,* 195 (1983).

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