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USE OF ALKALI CARBONATE AND ALKALI PHOSPHATE TO ELIMINATE INHIBITORY EFFECTS OF SOME IMPURITIES ON THE PRECIPITATION OF CALCIUM AND MAGNESIUM FROM PROCESS WASTE WATER[a,b]

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[a]Work performed at the Oak Ridge National Laboratory, operated by Union Carbide Corporation for the United States Atomic Energy Commission.

[b]This paper is for review by the Journal of the American Water Works Association.

[c]Radiation Applications, Incorporated, New York, N. Y.

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USE OF ALKALI CARBONATE AND ALKALI PHOSPHATE TO ELIMINATE INHIBITORY EFFECTS OF SOME IMPURITIES ON THE PRECIPITATION OF CALCIUM AND MAGNESIUM FROM PROCESS WASTE WATER [a,b]

Ernest Schonfeld [c]

ABSTRACT

Calcium in process waste water greatly reduces the efficiency of removal of radioactive strontium by two processes being studied at ORNL, namely, foam separation and ion exchange. For this reason, head-end precipitation of calcium is being studied. The effects of a number of impurities in low-activity process waste water (at the Oak Ridge National Laboratory) on precipitation of calcium and magnesium by the alkali-carbonate and alkali-phosphate methods are summarized in this report.

In tests with ORNL tap water as a substitute for process waste water, orthophosphate, hexametaphosphate, pyrophosphate, and tripolyphosphate (added as sodium salts to 1- or 1.5-ppm levels), Turco 4324, and "Fab" at the 3 ppm level individually reduced the rate of calcium carbonate precipitation from 0.01 M NaOH solution. This inhibitory effect was nearly eliminated by making the water 0.005 M in Na_2CO_3, 0.005 or 0.01 M in NaOH, and initially 4 ppm in ferric iron.

Impurities such as the pure detergent sodium dodecylbenzene sulfonate (at 2 to 50 ppm), fluoride (7 ppm), oxalate (3 ppm), and ethylenediamine tetraacetate (10 ppm), excluding the small fraction of calcium directly complexed by the latter, do not interfere with calcium carbonate precipitation.

Neither magnesium hydroxide precipitation in the alkali-carbonate process nor calcium phosphate precipitation in the alkali-phosphate process studied here were affected by any of the impurities.

Tests with eight samples of ORNL low-activity process waste water were in agreement with tests on tap water.

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INTRODUCTION

The purpose of this report is to describe the inhibitory effects (and their elimination) of some of the more common impurities on the precipitation of calcium and magnesium from process waste water. Because calcium is so similar to strontium (the element of special interest here) in many of its chemical reactions, it is first necessary to remove a major portion of it before the strontium concentration can later be reduced by a factor significantly greater than 10. Removal of the long-lived (28-yr half-life) strontium-90 from process waste water at nuclear energy installations is necessary to avoid increasing the concentration of this hazardous nuclide in streams and rivers.

Two processes are being studied at the Oak Ridge National Laboratory (ORNL) for removing strontium from process waste water, namely, ion exchange, with synthetic (1) and natural (2) exchangers, and foam separation (3). Each process is much more efficient in strontium removal if the calcium concentration is below 5 to 10 ppm, as calcium carbonate, rather than at the approximately 65-ppm level of the waste water. For this reason the precipitation of calcium in a head-end step was introduced at an early stage of these studies.

Two general methods for calcium precipitation are well known in the water-treatment industry (4), namely the lime-soda process, in which calcium precipitates as the carbonate, and the phosphate process, in which calcium precipitates as the orthophosphate. In both processes magnesium also precipitates as the hydroxide.

The rate of precipitation of calcium is very important when large volumes of water must be treated. Thus, when water from a water-treatment pilot plant at ORNL (5) showed widely varying concentrations of calcium, it became necessary to investigate the effects of impurities on the rate of calcium precipitation and on its steady-state concentration.

Impurities known to be present in ORNL waste water, excluding radioactive elements, are numerous. These include sodium hexametaphosphate, the decontaminating agent Turco 4324, commercial cleaning formulations, of which Fab is used extensively and which contain alkylbenzene sulfonates and various phosphates (6), fluorides, oxalates, and the chelating agent ethylenediamine tetraacetic acid (EDTA). (Turco 4324

is a proprietary formulation of Turco Products Inc., Wilmington, California. Chemical analyses at this laboratory showed it to contain phosphate convertible to PO_4^{3-} of 36.9%. Fab is a proprietary formulation of Colgate-Palmolive Company, New York. Chemical analyses at this laboratory were as follows: alkylbenzene sulfonate (ABS), 30%; total phosphate convertible to PO_4^{3-}, 28%.) Of these complexers, it is already known that sodium hexametaphosphate when present in concentrations of a few parts per million, greatly inhibits the rate of calcium carbonate precipitation (7). However, for our purposes, it was necessary to learn more about all these complexers.

The scope of this report includes studies of the effects of the above-named impurities and the elimination of these effects by modifications of both the lime-soda and alkali phosphate water softening processes. In some of the tests, the impurities were added to ORNL tap water to determine their individual effects on the final calcium concentrations. These results are pertinent because the process waste water has nearly the same gross composition as the tap water. In other tests, softening of process waste water, itself, with its variety of impurities and algae, was studied.

EXPERIMENTAL

Experiments reported here involved measuring the final concentration of dissolved calcium or calcium plus magnesium at 25 ± 1°C, after adjusting the water to one of the three modifications of the lime-soda process or one modification of the phosphate process as follows:

1. Water adjusted to 0.01 M NaOH, with and without 4 ppm Fe^{3+}.
2. Water adjusted to 0.005 M NaOH and 0.005 M Na_2CO_3, with and without 4 ppm Fe^{3+}.
3. Water adjusted to 0.01 M NaOH and 0.005 M Na_2CO_3, with and without 4 ppm Fe^{3+}.
4. Water adjusted to 0.004 M NaOH and 60 ppm PO_4^{3-}.

In each experiment 500 ml of water was adjusted to one of the above compositions and then stirred rapidly (in excess of 100 rpm) for 2 hr. At this point $FeCl_3$, as 2 ppm Fe^{3+}, was added as a coagulant in all experiments, and the stirring was reduced to a

low rate (about 20 rpm). At the end of a 15-min slow agitation period, the solution-slurry was centrifuged for 5 min, and the supernatant solution was decanted and acidified with hydrochloric acid to about 0.01 M to prevent further precipitation of calcium and magnesium. The acidified solutions were then analyzed for calcium and calcium plus magnesium.

Calcium was analyzed by photometric titration at 480 mμ and pH 12 with 0.00125 M tetrasodium ethylenediamine tetraacetate (Na_4EDTA), using murexide as indicator (8). Total hardness, which in this work is due nearly entirely to calcium and magnesium, was similarly determined but at 530 mμ, pH 10, and with erichrome black T as indicator (8). From tests with standard solutions prepared by adding known quantities of calcium carbonate (in 0.01 M HCl solution) to demineralized water, the limit of detectability and the reproducibility were ±0.2 ppm as calcium carbonate. For convenience the following conversion factors were used:

1. One ppm magnesium "as $CaCO_3$" = 0.243 ppm Mg.
2. One ppm calcium "as $CaCO_3$" = 0.400 ppm Ca.

RESULTS

Nine water samples were used in the tests, eight of which were low-activity waste samples, taken just upstream from the ORNL million-gallon equalization basin, and one of which was ORNL tap water. The low-activity process water does not differ grossly in composition from ORNL tap water (Table 1).

Results of these tests, which are presented in Table 2, may be summarized as follows. Adjusting ORNL tap water, with an initial total hardness (calcium plus magnesium calculated as calcium carbonate) of about 100 ppm, to 0.01 M in NaOH reduced the hardness to a few parts per million. However, in the presence of 1.5 to 3 ppm of Turco 4324, Fab, sodium hexametaphosphate, sodium pyrophosphate, and sodium orthophosphate the final hardness increased to the range 20 to 40 ppm. The addition of ferric iron as a coagulant had no beneficial effect in these cases. In addition, the surfactant sodium dodecylbenzene sulfonate at concentrations up to 50 ppm, ethylenediamine tetraacetate to 10 ppm (in which case it would be complexed with and retain about 2.7 ppm of

Table 1. Composition of ORNL Low-Activity Waste and Tap-Water

Sample	Date	Ca (ppm as $CaCO_3$)	Mg (ppm as $CaCO_3$)	pH	HCO_3^- (ppm)	Total P[a] as ppm of PO_4^{3-}
LAW 1	5/21/62	65	39	7.5	76	3.4
LAW 2	5/22/62	68	37	8.0	88	2.6
LAW 3	5/23/62	61	39	8.0	88	2.6
LAW 4	5/24/62	64	38	8.3	88	2.8
LAW 5	5/25/62	60	36	8.0	83	3.0
LAW 6	6/13/62	63	34	8.2	102	2.0
LAW 7	6/14/62	63	35	8.8	100	3.0
LAW 8	6/15/62	63	33	8.0	108	3.0
ORNL Tap		64	35	7.8	90	< 0.1

[a]In the analysis all phosphates were converted to the orthophosphate.

calcium (calculated as $CaCO_3$) in solution), ammonium oxalate to 3 ppm, sodium fluoride to 7 ppm F^-, and cupric copper, which was tested because it is a potential algae growth inhibitor, to 0.5 ppm, had no deleterious effect on the precipitation of calcium and magnesium from 0.01 M NaOH solution. Sodium tripolyphosphate, 1.5 ppm, has only a small effect on the final hardness.

The addition of sodium carbonate to the level 0.005 M greatly reduced the influence of the above-named impurities on the final concentration of calcium. Further, in those cases in which the dissolved calcium-plus-magnesium concentration was significantly greater than 5 ppm after hydroxide-carbonate treatment, the addition of ferric iron, generally at the 4 ppm level, reduced this dissolved calcium plus magnesium to the 4 to 5 ppm level. Iron did not have this beneficial effect in the hydroxide solutions.

Low-activity waste water at ORNL contains an average of about 2 ppm each of phosphate and alkylbenzene sulfonate under normal conditions due to the use of commercial detergents;[d] on occasion these concentrations can be in the range 3 to 5 ppm

[d]From analyses of Fab and its average usage and process water flow, its concentration is about 5 ppm, corresponding to 1.5 ppm each of phosphate and alkylbenzene sulfonate.

Table 2. Results of Beaker Tests of Interference in Calcium Precipitation[a]

	Final Hardness, as ppm $CaCO_3$, After Alkalizing to:					
	0.005 M Na_2CO_3, 0.005 M NaOH		0.01 M NaOH		0.005 M Na_2CO_3, 0.01 M NaOH	0.005 NaOH 60 ppm $PO_4^{\equiv}$
	Ca+Mg	Ca	Ca+Mg	Ca	Ca+Mg	Ca+Mg
ORNL Tap Water	5.9	2.9	3.5	3.4		
plus 3 ppm Turco 4324	7.2	3.9	28	25		
plus 3 ppm "Fab" (28% P as PO_4^{3-} equivalent)	10.0	7.0	36		4.3	6.5
plus 3 ppm "Fab" plus 4 ppm Fe^{3+}	4.1		30		4.8	
plus 2 ppm Na dodecylbenzene sulfonate	7.7	3.2	4.5	3.8		
plus 50 ppm Na dodecylbenzene sulfonate	6.9		5.6			
plus 1.5 ppm Na hexametaphosphate	11.0	8.5	21.0	18.0	4.2	6.5
plus 1.5 ppm Na hexametaphosphate plus 4 ppm Fe^{3+}	3.7		24.0		5.3	
plus 1.5 ppm Na tripolyphosphate	7.5	3.0	8.5	7.3		
plus 1.5 ppm Na pyrophosphate	10.0	5.0	16.0	15.0		
plus 1.0 ppm PO_4^{3-} (as Na_3PO_4)	15.3		34.0		25.2	5.3
plus 1.0 ppm PO_4^{3-} plus 4 ppm Fe^{3+}	4.0		51.0		13.4	
plus 10 ppm $Na_2EDTA \cdot 2H_2O$	6.6[x]		4.9[x]			5.9
plus 3 ppm Am oxalate	5.4		2.4			
plus 7 ppm F^- (as NaF)	6.9		4.6			5.7
plus 0.5 ppm Cu^{2+}	6.2		4.3			
plus 1.5 ppm Na hexametaphosphate plus 0.5 ppm Cu	18.1		37.0			
Low-Activity Waste, 1 (total P as PO_4^{3-} eq. 2.6 ppm)	17.4		49.0			
Low-Activity Waste, 2 (total P as PO_4^{3-} eq. 2.8 ppm)	13.1	9.6	56.0	50.0		
Low-Activity Waste, 3 (total P as PO_4^{3-} eq. 3 ppm)	16.1	13.4	36.0	35.0		5.1
Low-Activity Waste, 4 (total P as PO_4^{3-} eq. 3 ppm)	29.0		54.0			
Low-Activity Waste, 5 (total P as PO_4^{3-} eq. 3 ppm)	19.1		49			8.7
Low-Activity Waste, 4 plus 6 ppm Fe^{3+}	10.9					
Low-Activity Waste, 3 plus 25 ppm $Ca(OH)_2$	15.6	11.2	41	37.5		
(pH)	(11.3)		(~11.7)		(~11.8)	(~11.3)

[x] Non-complexed (Ca + Mg).

[a] See Table 1 for analyses of inlet water.

as a result of cleaning equipment. Tests with eight samples of this water that were representative of somewhat abnormal conditions (3 ppm of PO_4^{3-}) substantiated the advantage of using sodium carbonate and ferric iron to precipitate calcium carbonate (Table 2).

Generally speaking, precipitation of magnesium is not slowed by any of the impurities studied in this work. Whereas the initial magnesium concentration (initial total hardness minus initial calcium hardness) was about 30 ppm, its final concentration (final total hardness minus final calcium hardness) was reduced to 3 to 5 ppm in all experiments.

Beyond noting that none of the impurities, individually in ORNL tap water or as a composite in ORNL process waste water, affected the precipitation of calcium in 0.004 M NaOH — 60 ppm PO_4^{3-} medium, only two other comments are made. First, depending on the impurity, precipitation could be seen only after 5 to 15 min of agitation in the tests with sodium hydroxide or sodium hydroxide-sodium carbonate; on the other hand, turbidity was noticeable almost immediately in the phosphate precipitation tests. Second, although EDTA does not interfere with precipitation of calcium which it does not retain in solution as a complex, it does retain calcium to a value of 1 mole of calcium per mole of EDTA.

DISCUSSION

Some of the effects of phosphates on preventing precipitation of calcium carbonate are so large that the mechanism cannot be due primarily to homogeneous complex or chelate formation (7). For example, 1 ppm of PO_4^{3-}, equivalent to about 0.01 millimoles of PO_4^{3-} per liter, caused the retention of 30.5 ppm of calcium plus magnesium (that is 34.0 minus 3.5 from the tap water control test, rows 11 and 1, column 3 of Table 2), equivalent to about 0.30 millimole of these two elements per liter. Thus, in this particular case complex formation could account for only about 5% of the effect of the phosphate. The mechanism of the effect must, therefore, reside in kinetic and crystal growth factors.

Precipitation of calcium carbonate can be a very slow process. Its rate is proportional to the free surface area of calcium carbonate crystals and to the extent of

supersaturation of the Ca^{2+} and CO_3^{2-} ions (9,10). Thus, the rate of precipitation can be greatly increased if there is a high concentration of seed crystals. This was shown by the experiments of McCauley and Eliassen (11). It is also known (12) that orthophosphate will compete with carbonate in crystal growth, thereby producing a solid containing both calcium, carbonate, and phosphate, reducing the surface area available for further growth, and reducing the rate of precipitation (7). Other P(V) phosphates, such as the tripolyphosphate, hexametaphosphate, and pyrophosphate may act similarly. The fact that sodium carbonate greatly reduced the deleterious effects of phosphates on precipitation of calcium carbonate is consistent with such a mechanism. The effect of carbonate in reducing interference by phosphate in the present experiments can be viewed as a competitive or mass action effect. This is because the equivalent ratio $2(CO_3^{2-})/3(PO_4^{3-})$ is about 400 at the start of precipitation when 0.005 M CO_3^{2-} is added to a solution containing 80 to 90 ppm of dissolved bicarbonate, 0.005 M in NaOH, and 1 ppm of orthophosphate. In the absence of added carbonate the normal bicarbonate ion concentration in ORNL water (80 to 90 ppm) corresponds to the ratio (in the presence of 0.005 to 0.01 M NaOH) $2(CO_3^{2-})/3(PO_4^{3-})$ of only about 100.

When ferric iron is added to carbonate-caustic solutions a further reduction in the final soluble calcium concentration is observed, unless this concentration is already down to ~5 ppm, whereas the iron has essentially no effect in the absence of added carbonate. According to the model of Nesbitt, et al. (13), PO_4^{3-} and OH^- ions react with hydrous ferric oxide, thereby removing interfering phosphate and simultaneously producing a crystal surface with which Ca^{2+} ions can react. When phosphorus exists as the orthophosphate, iron is more necessary in the 0.005 M Na_2CO_3-0.005 M NaOH (pH 11.3) solution than in the 0.005 M Na_2CO_3-0.01 M NaOH (pH 11.8) solution to reduce the dissolved calcium content to its minimum value (under present experimental conditions) of about 3 ppm (as $CaCO_3$). This is probably due to the hydroxyl ion effect which is greater at pH 11.8 than at pH 11.3. It should be noted that under the more favorable conditions of sludge bed filtration (14), residual calcium hardness can be reduced to less than 1 ppm.

CONCLUSIONS

From the experiments discussed, the following conclusions may be derived:

1. Precipitation of calcium carbonate from ORNL tap water or low-activity process waste water made 0.01 M in NaOH is seriously inhibited by the presence of 1 to 1.5 ppm of hexametaphosphate, pyrophosphate, orthophosphate, and by the presence of 3 ppm Turco 4324 or Fab; tripolyphosphate has a small inhibitory effect.

2. The inhibitory effect of phosphate (at the 1 to 1.5 ppm level) on calcium precipitation can be overcome by making the water 0.005 M in Na_2CO_3, initially several parts per million in ferric iron, and at an NaOH concentration of 0.005 to 0.01 M. Addition of calcium carbonate seed crystals is also beneficial.

3. The following impurities, at the concentrations noted, do not interfere with the precipitation of calcium carbonate: the pure detergent sodium dodecylbenzene sulfonate (2 to 50 ppm); fluoride (7 ppm); ammonium oxalate (3 ppm); and ethylenediamine tetraacetate (10 ppm). This excludes the small fraction of calcium complexed by the ethylenediamine tetraacetate.

4. The precipitation of magnesium hydroxide was not inhibited by any of the impurities under the test conditions.

5. The precipitation of calcium as the phosphate from water made 0.004 M in NaOH and 60 ppm in PO_4^{3-} was not inhibited by any of the impurities. However, the precipitate was composed of smaller, slower settling particles than those obtained from precipitation of calcium as the carbonate.

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