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THE EFFECT OF SURFACE ACTIVE AGENTS ON DECONTAMINATION OF RADIOACTIVE AQUEOUS WASTES BY PRECIPITATION AND COAGULATION PROCESSES

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ABSTRACT

The effect of the presence of certain surface active agents on decontamination using the calcium/ferric phosphate process in a sludge blanket clarifier was investigated. Little trouble with such agents should be experienced in the treatment of effluent at Lucas Heights.

CONTENTS

1. INTRODUCTION

Using mains water as the influent, a series of inactive runs were made to find the effect of the presence of the surface acting agents (surfactants) Teepol, Lissapol, Turco 4182A, Calgon and E.D.T.A. on the coagulation of calcium and ferric phosphates under alkaline conditions in a sludge blanket clarifier. The agents were added continuously to the clarifier influent as described in Frost (1961) for radioactive solutions. Addition of the agents was accurate to within 6 per cent.

If certain concentrations of surfactants stabilise the colloidal particles, it is likely that radioactive decontamination will be affected at a similar concentration, so results from runs under inactive conditions were used as a guide in subsequent runs using radioactive effluent containing uranyl ions. Uranyl ions were chosen to assess the effect on decontamination because they are very effectively removed from solution by the phosphate process (Burns and Glueckauf, 1958) and give an overflow which is virtually inactive. If surfactants in the effluent stabilise the floc, activity will enter the overflow. If they produce soluble complexes with uranyl ions, the activity of the overflow will be increased. The activity in the overflow due to complexing may be distinguished from that due to floc stabilisation by centrifuging samples of the overflow.

The average concentration of surfactants in the effluent received for treatment is unlikely to exceed 100 p.p.m., so this was the maximum concentration used in the tests.

2. LITERATURE SURVEY

Previous work shows how detergents and complexing agents interfere with water treatment by coagulation.

Cross (1950) investigated by batch jar tests the effect of domestic and industrial synthetic detergents on the coagulation of Lake Michigan water using alum, ferric chloride, or ferric sulphate. Detergents were used in concentrations ranging from 0.1 to 5 p.p.m. Interference with coagulation occurred when the concentration was about 5 p.p.m. With all detergents the effect was minimised by raising the pH to 9.1 or higher.

Using standard jar tests, Langelier (1952) studied the effect of anionic, cationic, and non-ionic detergents and complexing agents on the coagulation of alum in synthetic turbid waters. With detergents, at a pH of 7.0, it was found that agents of the same type showed greatly variable effects; concentrations causing serious interference ranged from 17 p.p.m. to greater than 600 p.p.m. The deflocculation caused by the complexing agent sodium metaphosphate could be overcome by using greater quantities of alum coagulant but, as the concentration of the phosphate increased, the quality of the floc fell until with a concentration of 5.0 p.p.m. or more, normal alum flocculation could not be obtained regardless of the amount of alum added. Results with E.D.T.A. were similar to those obtained with metaphosphate except that more E.D.T.A. was required to produce the same effect and normal flocculation could be obtained, using sufficient alum, up to 170 p.p.m. E.D.T.A.

Jar tests using an aluminium sulphate–tannin coagulation at pH 10.9 were used by Cantel and Cohen (1957) to investigate the effect of several agents on the decontamination of two types of effluent:

(a) a solution of fission products at pH 1.6, and

(b) a representative sample of effluent arising from the plutonium factory at Marcoule.

Of the agents tested, some were detrimental, others had no effect, and some had an effect depending on the type of effluent. Five per cent. w/w E.D.T.A. did not affect the decontamination of effluent (b) though 500 p.p.m. E.D.T.A. affected the decontamination factor of effluent (a).

Christenson et al. (1951) studied the decontamination of Pu– containing effluent using ferric hydroxide precipitation, adjusting the pH with lime. Citric acid and various phosphate complexing compounds, including Calgon, were used in concentrations up to 400 p.p.m. These agents were found to have a marked effect on the flocculation and decontamination. The interference caused by all agents could be overcome by adding calcium ions and increasing the pH to 12.0. Two months operation of a pilot plant confirmed laboratory experiments.

The effects of E.D.T.A. described by Dejonghe and D'Hont (1957) involved jar tests using effluent containing Sr^{90} and Ru^{106}. They considered it unnecessary to alter the pH of the solutions to counteract the effect of E.D.T.A. which complexes many cations best under alkaline conditions. E.D.T.A. forms a soluble complex with strontium that is stable over a large pH range; it was found that 10 p.p.m. E.D.T.A. reduced the elimination of Sr^{90} from 98.5 per cent. to 52 per cent. Ru^{106} decontamination was little affected.

In summary, where troublesome effects are experienced due to the presence of various agents, they can be minimised by using a high pH environment.

3. RESULTS OF INACTIVE RUNS

In the series of inactive runs the concentration of each surfactant was increased in each experiment until difficulty in control of the clarifier was experienced. A maximum concentration of 100 p.p.m. was used, as discussed in Section 1. The results are shown in Table 1.

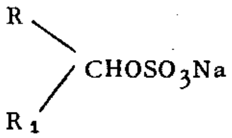
3.1 Lissapol

Lissapol is a non–ionic type of detergent formed by condensing ethylene oxide with a phenol derivative (McCutcheon, 1950).

No difficulty was experienced in building up a stable blanket and obtaining a clear overflow at the launder. As the concentration of Lissapol in the effluent increased, a deflocculation tendency caused mobility of the blanket but this was not troublesome. Lissapol caused much foaming in the central compartment. Analyses show that most of the Lissapol passed straight through the clarifier. This is feasible as Lissapol is non–ionic and should not be adsorbed in the diffuse double layer surrounding the primary particles. Some adventitious trapping of such large molecules in the solid lattices is to be expected and this occurs, as the Lissapol concentration falls when the effluent passes through the clarifier. The overflow calcium concentration in the first experiment is anomalously large, due to flow–rate errors. This also depresses the overflow pH.

3.2 Teepol

Teepol is much used in laboratories for cleaning apparatus. It is an anionic detergent, a secondary alcohol sulphate of the form



$$\begin{matrix} R \\ & \!\!\!\!\!\!\searrow \\ & & CHOSO_3Na \\ & \!\!\!\!\!\!\nearrow \\ R_1 \end{matrix}$$

which is delivered as a 20 per cent. w/w strength solution. This was diluted to give a suitable concentration for each experiment. Table 1 shows the chemical analyses for each run.

No trouble was experienced in building up a blanket or keeping it stable, though the mobility of the floc in the blanket increased with rising concentration of Teepol.

The particles precipitated are partially hydrophobic and flocculation occurs despite the hydrophobic portion of the Teepol molecule being preferentially attracted. The ionic portion of the Teepol molecule is electrostatically attracted by the floc. The combination of these effects leads to the trapping of about 70 per cent. of the Teepol in the sludge blanket.

3.3 Calgon

Calgon is marketed in many forms and can be represented by the formula $(NaPO_3)_6$. Its characteristics are strong sequestering action (forming water soluble metal complexes) as well as strong dispersing and deflocculating action. Concentrations of calcium given in Table 1 include free and complexed calcium.

Up to a concentration of 25 p.p.m. Calgon, the clarifier overflow was not noticeably coloured, but at 42 p.p.m. concentration the overflow, though clear, was yellowish in colour. Next day a sample of this overflow was colourless but floc had settled out, showing that the colouration was due to colloidal basic ferric phosphate sols stabilised by the Calgon. This is verified by the analyses for the last run, where the Fe^{+++} and PO_4^{---} concentrations increased. The concentration of ferric ions in all these runs was higher than in runs with other agents, due to small quantities of stabilised sols being in the overflow. The concentration of phosphate is excessively high in these runs; this may be due to errors in phosphate ion feed rates, but more probably due to decomposition of Calgon complexes (Norwood, 1955), which break down to meta- and ortho-phosphates. Only small quantities of Calgon pass through the blanket due to trapping of the large ionic calgon molecules.

3.4 E.D.T.A.

In this work, the disodium salt of ethylene diamine tetra-acetic acid was used. This salt ionises:

$$Na_2YH_2 \rightleftharpoons 2Na^+ + H_2Y^{--}$$

It is a very powerful agent forming, practically instantaneously, 1:1 complexes with most cations, regardless of their oxidation state, i.e.

$$H_2Y^{--} + M^{n+} \rightarrow MY^{(n-4)} + 2H^+ .$$

Complex formation depends on the pH value of the solution; E.D.T.A. complexes ions most efficiently in basic environments such as those used in phosphate coagulation.

No difficulty in developing and maintaining a stable blanket was experienced at concentrations up to 15 p.p.m. E.D.T.A. 20 p.p.m. E.D.T.A. proved harmful to the blanket, the supernate being a yellowish colour. The difference between the analyses of the unfiltered and filtered effluent shows the large quantity of floc entrained.

E.D.T.A. complexes cations, which therefore cannot combine with phosphate ions. This results in an excess of phosphate ions in the overflow from the clarifier, which increases as the concentration of influent E.D.T.A. rises.

The results show that all the E.D.T.A. was complexed. Under the pH conditions employed, only Ca^{++} would react with the E.D.T.A. As the analyses show, most of the complex was trapped by the blanket. The iron concentration in the overflow increased with rising E.D.T.A. concentration, due probably to increasing stability of ferric phosphate sols. The pH also rose through the series of runs. This is probably due to the increasing concentration of phosphate ions PO_4^{---} which would tend to raise the pH.

3.5 Turco 4182A

Turco 4182A is a mixture of detergent and water softening agents (Norwood, 1955). Its salt composition consists of phosphate, carbonate and ammonium ions. It is a very good clothing decontamination agent. Its composition was not known when these experiments were carried out so no analyses were made.

Using this material, the floc particles would not aggregate as well as with Teepol or Lissapol, but 100 p.p.m. Turco 4182A was introduced at pH 11.5 without preventing the establishment of a stable blanket, even though it was very mobile, with disturbances developing (Figure 1).

4. DISCUSSION OF RESULTS FROM INACTIVE RUNS

Experiments showed that detergents and complexing agents adversely affect flocculation.

The mechanism of interference by detergents is that the hydrophobic part of the molecule is preferentially attracted to the partially hydrophobic solid floc particles and the molecules surrounding the particles form an insulating layer that reduces aggregation. The degree of the effect of detergents varies because they all have different hydrophobic-hydrophilic balances and behave differently under different conditions.

Complexing agents deflocculate by a different mechanism; they are multivalent and form soluble complexes with available cations. The residual cations will be adsorbed in the counter ion layer, but the zeta potential will be greater than with no complexing agents and there may be sufficient repulsion between colloidal particles to hinder or even prevent flocculation depending on the concentration of complexing agents added.

From Section 2 it is apparent that a high pH value overcomes the deflocculating effects of detergents and complexing agents. A possible reason for this effect is as follows:

When the primary particle is formed under alkaline conditions, it is negatively charged. The negative ions which will be mainly adsorbed in the potential determining layer are PO_4^{---} and OH^- ions. In the counter-ion layer, positively charged ions are adsorbed and tend to reduce the zeta potential. As the pH increases and the concentration of OH^- ions rises, the electrical charge on the colloidal particle approaches a maximum at a rapidly decreasing rate. The concentration of Na^+ ions, added with the NaOH, increases until at high pH values adsorption of Na^+ ions is great enough to lower the zeta potential of the particles and the sols flocculate more readily (neglecting double-layer compression and other minor effects).

5. RESULTS OF ACTIVE RUNS

The radioactive solution was a $(U^{233}O_2)^{++}$ traced natural uranyl nitrate solution (1 g/l) fed continuously into the effluent to give an activity of 43 dis/(min)(ml). Analyses of the runs are given in Table 2.

In these experiments, results from the inactive runs were used as a guide. Where agents caused instability of the blanket (e.g. E.D.T.A., Calgon), two concentrations, one below and one above the critical concentration were used. Where agents (e.g. Lissapol and Turco 4182A) were not detrimental to clarifier operation, a concentration of 100 p.p.m. was used.

5.1 Lissapol

When using a Lissapol concentration of about 94 p.p.m., clarifier operation was stable. The analyses confirm this statement. All samples of the clarifier overflow were quite clear and the activity in the overflow at each pH value was extremely low showing that no sequestering of UO_2^{++} ions occurred.

5.2 Calgon

In the last run using 25 p.p.m. Calgon at a pH of 11.6, some instability of the blanket caused the uncentrifuged overflow to be slightly active. From the activity of the centrifuged overflow samples, there is negligible complexing of uranyl ions at a concentration of 25 p.p.m. Calgon.

In both runs using 42 p.p.m. Calgon the clarifier overflow was a yellowish brown colour due to the stabilisation of phosphate sols. The difference between the activity of the centrifuged and uncentrifuged samples illustrates this. The activity in the centrifuged samples is due to uranyl ions complexed by Calgon.

5.3 E.D.T.A.

Using 15 p.p.m. E.D.T.A. with U^{233} traced effluent a crystal clear overflow was produced as in the inactive runs. Runs using 28 p.p.m. E.D.T.A. were much easier to control than expected. In one, at pH 11.5, some instability of the blanket occurred as shown by the activity of the uncentrifuged overflow but in the other run the floc aggregated satisfactorily.

5.4 Turco 4182A

Previously at a pH of 11.5 it was found that 100 p.p.m. Turco 4182A made the blanket barely stable, due to floc stabilisation. Runs at a lower pH, using 102 p.p.m. of this agent showed in each case that the floc stabilisation made the blanket quite unmanageable, resulting in the high activity of the uncentrifuged overflow samples due to floc entrainment. The activity of the centrifuged samples is also high, showing that significant sequestering of uranyl ions occurred. This activity fell as the pH rose.

6. DISCUSSION OF RESULTS FROM ACTIVE RUNS

Only when using Turco 4182A were the results dependent on pH; the instability was great at lower pH values and the improvement as the pH was raised was significant both in clarifier operation and activity in the overflow. With Calgon and E.D.T.A. probably the pH range was too small to make any difference. While some instability occurred with 28 p.p.m. E.D.T.A., as shown by the analyses, it was much less than that experienced with 20 p.p.m. E.D.T.A. in the inactive runs. This difference is probably due to more experience having been gained in the operation of the clarifier; it had previously been observed that a very thick blanket helped to suppress instability.

100 p.p.m. Lissapol had no effect on the decontamination and probably the fact that 100 p.p.m. Teepol did not affect operation in the inactive runs applies to decontamination also.

Though the effects of surfactants noted were obtained when using the calcium/ferric phosphate process it is considered that the results could be used as a guide when using the aluminium hydroxide process, as both processes take place under alkaline conditions.

7. CONCLUSIONS

(1) 100 p.p.m. Lissapol in a radioactive effluent will not affect the decontamination at pH values greater than 10.1.

(2) 100 p.p.m. Turco 4182A in an effluent is too great for stable sludge blanket clarifier operation, though the instability can be mitigated by the use of higher pH values.

(3) 25 p.p.m. Calgon in an effluent is not detrimental to decontamination at pH values greater than 11.4 but 42 p.p.m. Calgon definitely stabilises floc, to make control of the clarifier difficult, and also complexes uranyl ions. It would form complexes with other radioactive ions.

(4) 16 p.p.m. E.D.T.A. in an effluent does not affect the decontamination but 28 p.p.m. makes clarifier control difficult and reduces the decontamination at a pH of about 11.

(5) Despite the sol stabilisation noted with complexing agents, only Turco 4182A reduced the decontamination to below 80 per cent. so that at the expected concentrations in the total site effluent, little trouble from these agents should be experienced.

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TABLE 1

Results of Inactive Runs

Surface Active Agent	Clarifier Influent		Clarifier Effluent						
			Unfiltered					Filtered	
	Conc. of Agent p.p.m.	pH	pH	Conc.of Agent p.p.m.	Ca^{++} Conc. p.p.m.	Fe^{+++} Conc. p.p.m.	PO_4^{---} Conc. p.p.m.	Ca^{++} Conc. p.p.m.	PO_4^{---} Conc. p.p.m.
Lissapol 1	20	11.5	8.6	4.6	10.9	0.4	4.9		
2	50	11.4	10.0	45.0	3.6	0.1	4.4		
3	100	11.5	10.0	84.0	4.6	0.1	4.2		
Teepol 1	9.8		9.8	1.58	5.6	0.1	3.72		
2	49	11.2	10.4	19.9	3.6	0.1	2.5		
3	98	11.4	10.3	37.8	2.8	0.1	5.5		
Calgon 1	8.4	11.4	10.3	0.5	3.0	0.8	7.7		
2	25.4	11.4	10.8	1.1	3.7	1.3	8.8		
3	42.2		9.9	1.5	3.5	3.8	11.6		
E.D.T.A. 1	5		9.3	0	1.0	0.32	7.1		
2	10		9.9	0	1.0	0.56	10.4		
3	15	11.4	10.7	0	1.0	0.64	24.2		
4	20	11.5	11.2	0	7.62	2.2	140.8	1.0	55.0

TABLE 2

Results of Active Runs

Run No.	Detergent	Detergent Conc. p.p.m.	pH	Activity in Overflow dis/(min)(ml)		Activity Removal %	
				Uncentrifuged	Centrifuged	Uncentrifuged	Centrifuged
1	Lissapol	94.6	10.1	0.98 ± 300%	0.98 ± 300%	98.0	98.0
2		94.2	11.0	1.8 ± 170%	1.8 ± 170%	95.7	95.7
3		93.6	11.5	1.8 ± 350%	0.8 ± 350%	98.0	98.0
4	Calgon	24.5	11.4	0	0	100	100
5		24.5	11.5	0.59 ± 480%	0.59 ± 480%	98.5	98.5
6		24.5	11.6	2.12 ± 130%	0.71 ± 330%	95.0	98.4
7		42.2	10.6	5.53 ± 57%	3.53 ± 79%	87.1	91.7
8		42.0	11.1	9.53 ± 41%	2.59 ± 105%	77.8	93.8
9	E.D.T.A.	16.2	10.35	1.18 ± 200%	1.18 ± 200%	97.0	97.0
10		16.1	11.0	0.71 ± 260%	0.71 ± 260%	98.4	98.4
11		16.0	11.1	1.18 ± 240%	1.18 ± 240%	97.0	97.0
12		28.3	10.8	3.06 ± 87%	3.06 ± 87%	91.5	92.7
13		28.3	11.3	6.82 ± 59%	5.4 ± 69%	84.0	87.4
14	Turco 4182A	102.8	10.4	Greater than influent activity	26.9 ± 24%	0	36.0
15		102.6	11.1		8.6 ± 45%	0	80.0
16		102.4	11.4	12.5	5.1 ± 67%	70.9	88.0

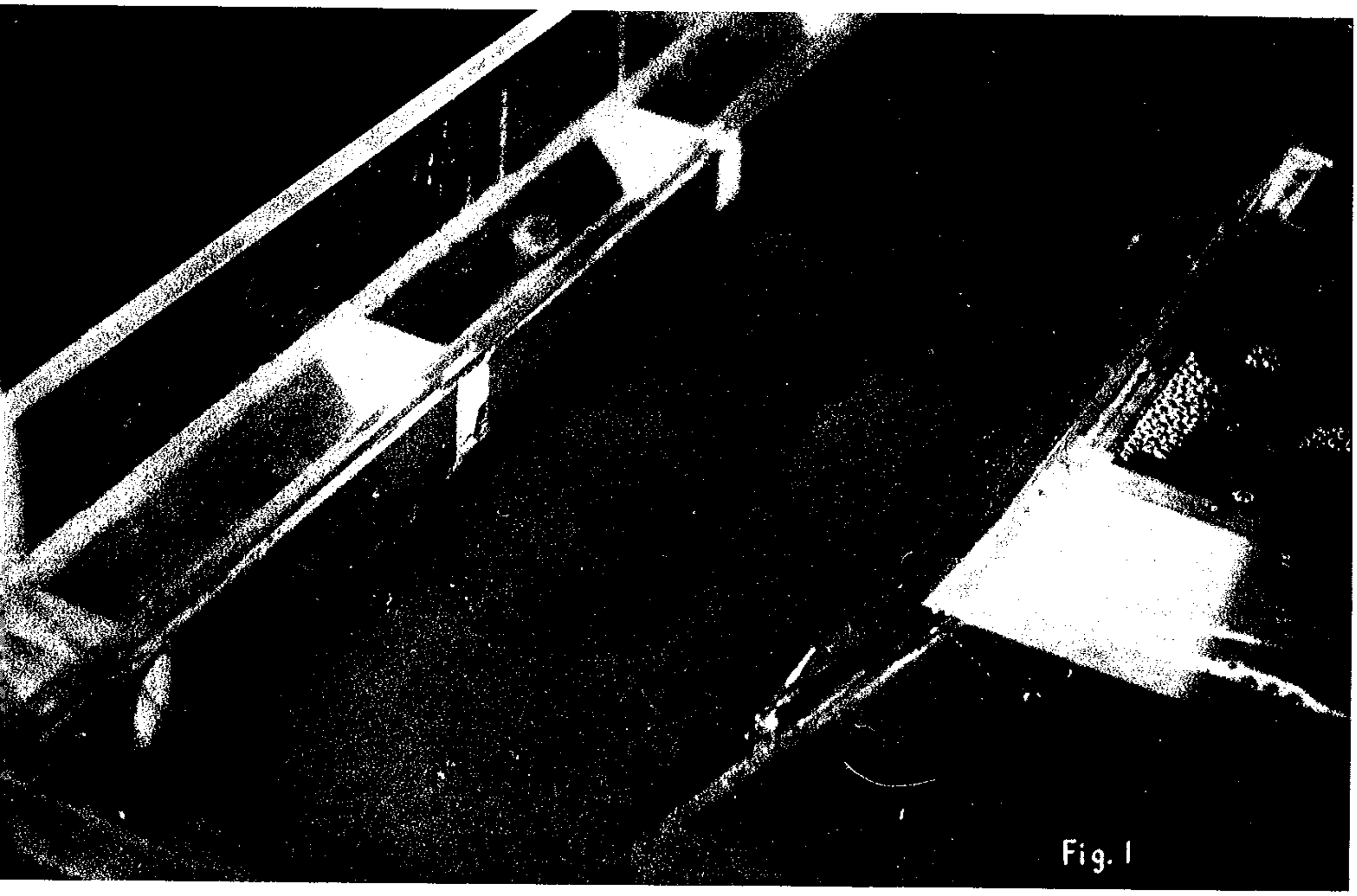

FIGURE 1. SLUDGE BLANKET IN THE PRESENCE OF 100 p.p.m. TURCO 4182A