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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

THE DECONTAMINATION OF SYNTHETIC EFFLUENT BY FLOTATION

by

R. LOPES CARDOZO

1963

Joint Nuclear Research Center
Ispra Establishment - Italy

Materials Department
Chemistry

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The volume of the foamate, after foam desintegration, was about 0.01 % of the volume of the treated water.

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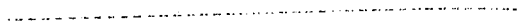

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CONTENTS

THE DECONTAMINATION OF SYNTHETIC EFFLUENT BY FLOTATION

SUMMARY

It is shown that flotation, both of sludges and of ions, may present a useful way for the decontamination of radioactive effluent.

In this preliminary work, decontamination factors of more than 25 for Cs, of more than 200 for Eu and of about 1.5 for Sr were obtained.

The volume of the foamate, after foam desintegration, was about 0.01 % of the volume of the treated water.

1 — INTRODUCTION

The aim of the treatment of radioactive effluent is to obtain the radioactive products in a small volume for easy and economic storage and to obtain a level of radioactivity in the treated water low enough for discharge in natural surroundings.

On a plant scale, the treatment consists at the moment usually out of one or two chemical flocculations, followed by ion exchange on cheap materials. The initial sludge with the bulk of the radioactive products needs further treatment in order to obtain the small volume for storage. Dejonghe and coworkers([1]) report plant scale results of two consecutive flocculations giving a decontamination of low active effluent between 85 - 97 % for aged mixed fission products (m.f.p.). These values were improved by a lignite ion exchange step to 98 - 99.4 %.

A simplification is reported by Clark([2]) who combines the two flocculations in one with somewhat lower decontamination.

A main objective against flocculation is that the flocs settle under gravity influence only, which gives voluminous settling tanks with a long residence time.

The result is a high initial sludge volume of about 5 % of the volume of the treated effluent, and a solid content of around 1 %. The volume is much too high for storage, but by a sequence of decanting, freezing and filtration, it can be reduced about fiftyfold.

Resuming, it can be said that the flocculation method is satisfactory from the point of decontamination, but it is a tedious operation.

Fundamentally different methods are needed, to obtain a better and faster floc removal, an easier sludge treatment and small sludge volume.

One of the possibilities is to remove the floc by flotation. This method will be more closely considered hereafter.

2 — THE FLOTATION METHOD

The flotation technique is a well known operation, mostly used in mineral technology to separate one mineral from another.

Recently attention was given to the use of this technique for the separation of ions and chemical flocs from aqueous solutions.

Sebba[3] reports the concentration of inorganic ions from aqueous solutions with specific foams. A surfactant ion, of charge opposite to the charge of the ion to be separated, is added to the solution and by air bubbling, a scum or froth is obtained containing a certain portion of the ions. Similar work is reported by Schonfeld and coworkers[4] on the removal of cations from dilute ($10^{-6} \rightarrow 10^{-5}$ M) solutions by adsorption on foam surfaces. By using specific surfactants decontamination factors of 400 → 700 were obtained for Sr and Sm in a single pass through a 1 m foam column and factors over 10^7 by 3 or four passes. It was found that the specific action of the surfactant is of great importance. DBDTTA*) was found to be specific for Sr and Deriphat 160**) for Sm. Similar data are given in a report of the same study group[5]. The above mentioned studies were only centered on the removal of radioactive products by foam separation alone and dealed not with any form of classical treatment.

It is also possible to use flotation as a means to reduce the volume of the sludge obtained from a chemical treatment. This method is described by Voznesenskii and coworkers[6] who report that ferric hydroxide could be floated. The technique used was first a normal flocculation with subsequent coagulation and transfer of the precipitate in a flotation cell. During flotation practically no desorption of the adsorbed ions takes place. Decontaminations of 64 % for Ru, 93.5 % for Sr and 99 % for Zr and rare earth cations are reported.

The two methods given above and called furtheron respectively ion flotation and sludge flotation, seem to be adaptable for effluent treatment.

In the following some experiments will be reported on ion flotation and sludge flotation separately and in combination.

3 — EXPERIMENTAL

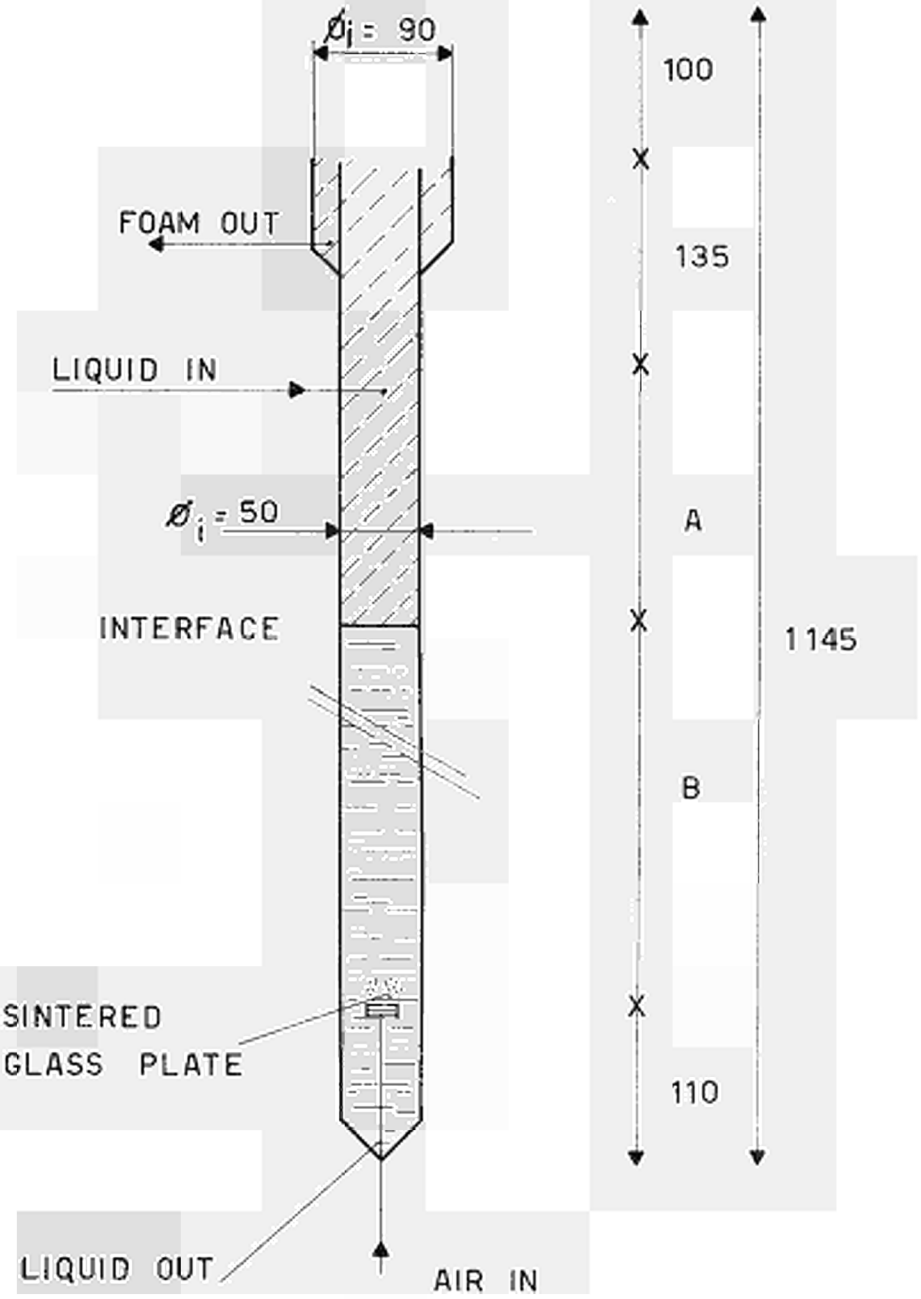
3.1 — General

Although an economic evaluation of the flotation method cannot be given now, it is believed that the method can only be competitive with flocculation if cheap surfactants can be used. It was thus decided to use generally available surfactants such as :

— sodium lauryl sulphate***) as prototype of the anionic surfactants,

*) Dodecyl-benzyl-diethylene-triamine-tetracetic acid.
**) $C_{11}H_{23}N(CH_2\text{-}CH_2COONa)_2$.
***) $C_{11}H_{23}\text{-}CH_2\text{-}SO_4\text{-}Na$.

FIGURE 3.1.I



FLOTATION CELL

A = DISTANCE FROM LIQUID INLET

B = " " " AIR "

SCALE 1:5

— Sapamine KW*) as cationic surfactant. Two other surfactants, n-octylamine and sodium laurate were found to be useless under the experimental conditions fixed in this work.

It was believed that the search for optimum experimental conditions was not yet opportune so that the conditions were more or less chosen at random.

The runs were carried out in the apparatus shown in Figure 3.1.I. The synthetic effluent was made up from distilled water (A.D.) or tap water (T.W.) containing 30 → 40 ppm Ca. Tracers were added of the order of $10^{-2}\mu$C/ml for Cs^{134} and Sr^{89} and $10^{-3}\mu$C/ml for Eu^{152} and m.f.p. Sometimes also 1 ppm of carrier was added.

In the first experiments, the surfactant was added to the liquor to be decontaminated, but during the sludge flotation runs it was observed that the formation of the floc was hindered by the surfactant. It was decided to introduce the surfactant separately at a calculated rate to obtain mostly the desired concentration of 25 ppm.

The variation in the column set-up consisted in a displacement of the foam/liquid interface and foam column height, as indicated by the values of A and B (Figure 3.1.I. and Tables 3.1.I., 3.2.I. and 3.3.I.).

The liquid flow rate was kept constant at 0.7 m/hr, the air flow rate 1 m/hr (A.D.) and 1.55 m/hr (T.W.). Under these conditions, stable foam columns were obtained, although sometimes the foam collapsed precociously when T.W. was used, due to a partial precipitation of the surfactant by the Ca-ions. It was not felt opportune to investigate the possibilities of the addition of foam stabilizers in this stage of the research.

All the runs lasted two hours at a minimum. Since it was found that the flotation was at equilibrium after about one hour of operation, see Figure 3.1.II., the results were calculated from samples taken around the second hour. The decontamination factors given are average values of two or more runs, except those given without a traject of probable error.

The reference flocculations were carried out in beakers, where the reaction was allowed to take place under 5' rapid stirring and 25' slow stirring. The solutions were directly centrifuged and counted.

3.2 — Sludge flotation

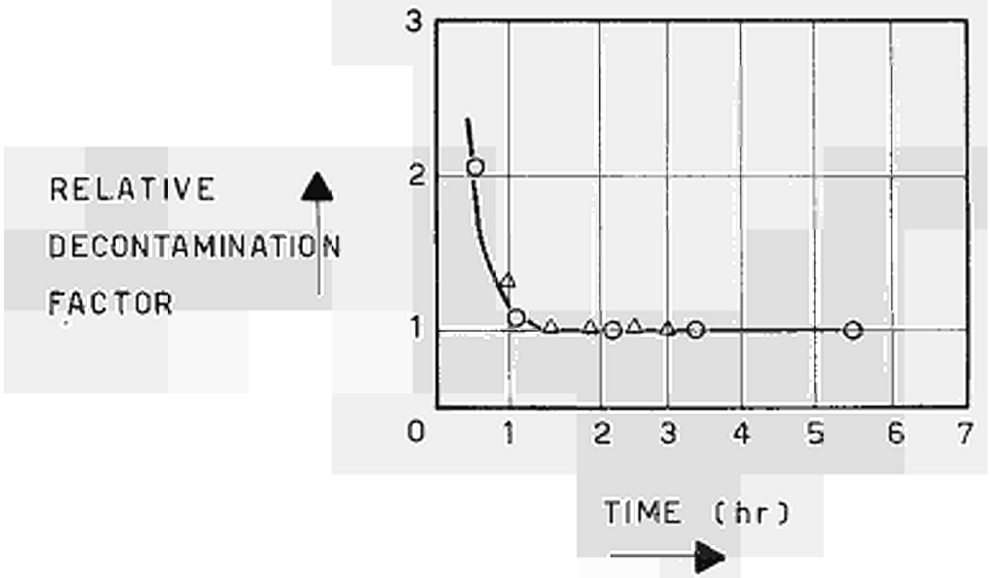
Sapamine KW was taken as surfactant since it is a cationic surfactant and thus without influence on cations.

At first, a ferric hydroxide precipitate was floated at pH 9 → 12. The floatability of the flocs was depending on the nature of the flocs before flotation. A satisfactory flotation, this is a clear effluent with more than 90 % of the Fe removed, was only obtained if the flocs were initially very small. With copperferrocyanide, always a completely clear filtrate was obtained. Calcium oxalate could not completely be removed from the solution.

The decontamination of m.p.f. by sludge flotation gives the same or better results compared with the reference flocculations.

*) Diethyl-amino-ethyl-stearylamide-hydroacetate.

FIGURE 3 1 II



RELATIVE DECONTAMINATION FACTOR OF FLOTATION RUNS VS TIME.
AVERAGE VALUES FROM TWO RUNS.

TABLE 3.2.1

Sludge flotation

Runs with 25 ppm Sapamine KW in A.D. Tracer : aged m.f.p.

Air flow rate 1 m/hr, liquid flow rate 0.7 m/hr except run no. 2 where the liquid flow rate was 0.4 → 1.6 m/hr.

	1	2	3	4	5
Flotation	—	+	—	+	+
Flocculation	+	—	+	—	—
Interface A (cm)	—	0	—	60	60
B (cm)	—	45	—	20	20
Surfactant added in liquor	—	+	—	—	—
at A = 25 cm	—	—	—	+	+
pH	11.5	9 - 12	6	6	7.6
Fe^{3+} (ppm)	18	18 - 27	—	—	—
$Fe(CN)_6^{4-}$ (ppm)	—	—	15.1	15.1	15 - 20
Cu^{2+} (ppm)	—	—	11.5	11.5	12
$C_2O_4^{2-}$ (ppm)	—	—	—	—	75 - 150
Ca^{2+} (ppm)	—	—	—	—	50
Decontamination factor D	2.5	2.5 - 4	2.2	2.5	4.6±0.4
Ibid. D_{Sr}	—	—	—	1.8	2.5
Ibid. D_{Cs}	—	—	—	2.5	5

3.3 — Ion flotation

Sodium lauryl sulphate (Nals) was chosen as anionic surfactant for the flotation of Cs, Sr and Eu.

The experimental conditions are given in Table 3.3.I.

TABLE 3.3.1

Ion flotation

Runs with 25 ppm Nals. Foam/liquid interface : A = 60 cm, B = 20 cm.

Feed : A.D., pH = 2. Surfactant added at A = 25 cm.

Air flow rate : 1 m/hr, liquid flow rate : 0.7 m/hr.

Run	Tracer	Carrier	Decontamination factor
1	Cs^{134}	—	1.4±0.2
2	»	1 ppm	1.09±0.04
3	Sr^{89}	—	2.5±0.5
4	»	1 ppm	2.4±0.1
5	Eu^{152}	—	330±150
6	»	1 ppm	400±90

The choice of the pH was based on the following :

— at pH = 2, the ions to be removed are in the ionic state and most likely not present as "radio-colloids";

— Nals gave a dry and stable foam at pH values between 1 and 3.

The conclusion of this series of tests is that trivalent ions are very well floated, the others markedly less. The influence of 1 ppm carrier is negligable. It appears furthermore that separation of rare earth cations from Sr and Cs may be effected by ion flotation. Similar results are reported by Schonfeld and coworkers([4]) on the Cs - Sr and Sr - Sm systems.

3.4 — The combined flotation

Since it appeared that both ion and sludge flotation were possible under certain circumstances, it was decided to investigate the possibilities of the combined operation. The main attention was given to foam stability, precipitate recovery and foamate volume. The pH was kept at a value of 2 where Nals gives a stable and dry foam. The results obtained with the combination Nals - copper ferrocyanide are summarized in Table 3.4.I. The data are average values of two or more runs.

It follows that the (ion) flotation of Eu and the (sludge) flotation of Cs are satisfactorely. The flotation of Sr is of practically no value. In general, the flotation runs show equal or better results than the reference flocculations.

It is noted that the results are somewhat favoured by the use of A.D. mostly. T.W. presented difficulties by giving unstable foam.

It is well understood that the flotation, before it will be operational, will need much work.

TABLE 3.4.1

Combined flotation

Flotation : 25 ppm Nals added at A = 25 cm, pH = 2, liquid flow rate : 0.7 m/hr, 15.1 ppm $Fe(CN)_6^{4-}$, 11.5 ppm Cu^{2+}.

Flocculation : solutions as above, contact time 0.5 hr.

Run	Air flow rate (m/hr)	Water used	Tracer	Carrier (ppm)	Decontamination factor	
					Flotation	Flocculation
1	1.0	A.D.	Cs^{134}	—	375±125	150±50
2	1.0	A.D.	Cs^{134}	1	90±30	45±20
3	1.55	T.W.	Cs^{134}	—	25± 6	32± 6
4	1.0	A.D.	Sr^{89}	—	1.7±0.3	1.4±0.1
5	1.0	A.D.	Sr^{89}	1	1.3±0.2	1.1±0.1
6	1.0	A.D.	Eu^{152}	—	200± 60	1.6±0.2
7	1.0	A.D.	Eu^{152}	1	750±250	1.1±0.0
8	1.0	A.D.	m.f.p.	—	5.7±0.7	2.0±0.1

3.5 — The volume of the foamate

An important feature of the flotation is that the foam volume, after foam desintegration, is mostly extremely small. The quantity of foamate leaving the flotation cell depends on several factors, such as air flow rate, surfactant concentration etc... It has been found that increasing the foam column height decreases the foamate volume.

A distribution of the obtained foamate volumes is given in Figure 3.5.I., valid for Nals at pH = 2 and a foam column of 60 cm. No differences could be observed between A.D. and T.W.

The further treatment of the desintegrated foamate, appearing as an oily suspension of sludge and surfactant, can consist of direct insolubilization or storage. It is noted, that the foamate dries upon standing in air. The tedious treatment necessary with the sludge from classical flocculation is anyhow not necessary here.

4 — CONCLUSION

Although many problems are not yet solved and many experimental difficulties are present, it seems that the flotation technique can be used for the decontamination of radioactive effluents.

Advantages of the method are that it is a one-step operation giving an extremely low sludge volume. Unknown at the moment are several factors such as :

— the influence of organic matter,

— the influences of liquid and gas flow rates,

— the use of foam stabilizers etc...

5 — NOTATION

A : distance from liquid inlet (Figure 3.1.I.) (cm)

B : distance from air inlet (Figure 3.1.I.) (cm)

D : decontamination factor

A.D. : distilled water

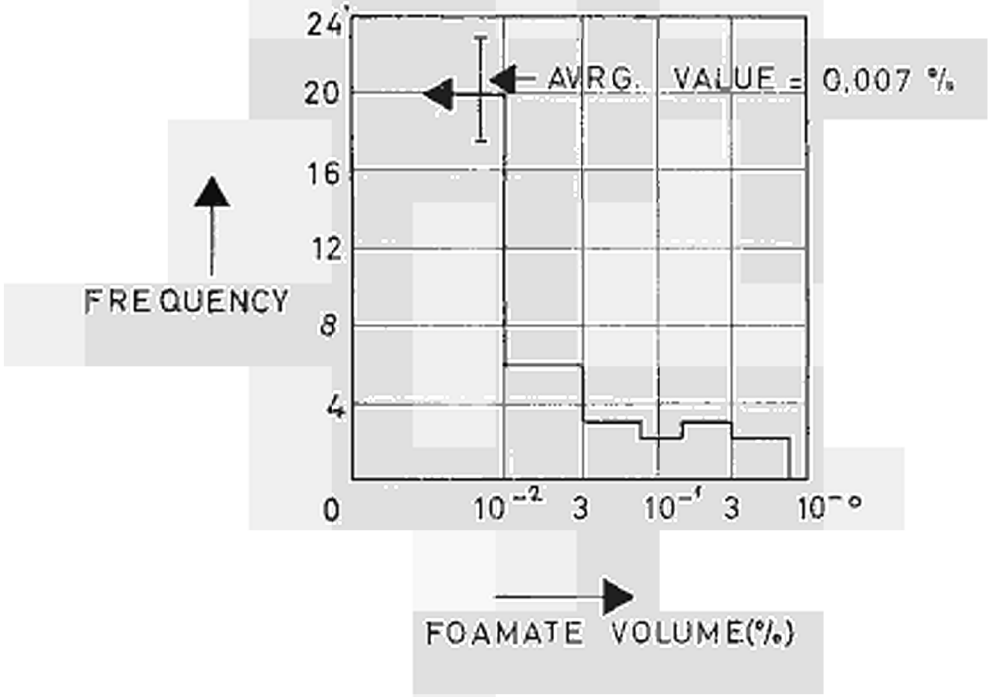
m.f.p. : aged mixed fission products

Nals : sodium lauryl sulphate

T.W. : tap water

FIGURE 3.5.I

FREQUENCY OF THE FOAMATE VOLUME



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