

EUR 4401 e

EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

**ZETA POTENTIAL CONTROL APPLIED
TO THE TREATMENT OF RADIOACTIVE EFFLUENT**

by

A. J. GILLOT-STOKKINK and R. LOPES CARDOZO

1969



**Joint Nuclear Research Center
Ispra Establishment — Italy**

**Chemistry Department
Organic Chemistry**

LEGAL NOTICE

This document was prepared under the sponsorship of the Commission of the European Communities.

Neither the Commission of the European Communities, its contractors nor any person acting on their behalf:

make any warranty or representation, express or implied, with respect to the accuracy, completeness or usefulness of the information contained in this document, or that the use of any information, apparatus, method or process disclosed in this document may not infringe privately owned rights; or

assume any liability with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

This report is on sale at the addresses listed on cover page 4

at the price of FF 7.75	FB 70.—	DM 5.10	Lit. 870	Fl. 5.10
-------------------------	---------	---------	----------	----------

When ordering, please quote the EUR number and the title which are indicated on the cover of each report.

Printed by Van Muyswinkel
Brussels, November 1969.

This document was reproduced on the basis of the best available copy.

EUR 4401 e

ZETA POTENTIAL CONTROL APPLIED TO THE TREATMENT OF RADIOACTIVE EFFLUENT, by A.J. GILLOT-STOKKINK and R. LOPES CARDOZO

European Atomic Energy Community — EURATOM
Joint Nuclear Research Center — Ispra Establishment (Italy)
Chemistry Department — Organic Chemistry
Luxembourg, November 1969 — 46 pages — 17 figures — FB 70

The aim of the present study was the improvement of working conditions in the decontamination plant for radioactive effluent at Ispra. This plant operates by a scavenging-flocculation process. The generally applied but unprecise "beaker tests" used for sedimentation control were completed by precise measurements of the surface charge or zeta potential of the radioactive sludge suspensions. This allowed the exact choice of appropriate reactants and dose rates for optimum flocculation in the case of each type of effluent to be

EUR 4401 e

ZETA POTENTIAL CONTROL APPLIED TO THE TREATMENT OF RADIOACTIVE EFFLUENT, by A.J. GILLOT-STOKKINK and R. LOPES CARDOZO

European Atomic Energy Community — EURATOM
Joint Nuclear Research Center — Ispra Establishment (Italy)
Chemistry Department — Organic Chemistry
Luxembourg, November 1969 — 46 pages — 17 figures — FB 70

The aim of the present study was the improvement of working conditions in the decontamination plant for radioactive effluent at Ispra. This plant operates by a scavenging-flocculation process. The generally applied but unprecise "beaker tests" used for sedimentation control were completed by precise measurements of the surface charge or zeta potential of the radioactive sludge suspensions. This allowed the exact choice of appropriate reactants and dose rates for optimum flocculation in the case of each type of effluent to be

treated. Zeta potential measurements were performed with a commercialised device called "Zeta-meter", comprising a Riddick-type electrophoresis cell.

The use of a cationic polyelectrolyte flocculant, such as the Purifloc C 31 of Dow Chemicals, has given very satisfying results. Its application in the decontamination plant produced excellent and stable settling conditions which resulted in doubling the previously obtained process rates.

treated. Zeta potential measurements were performed with a commercialised device called "Zeta-meter", comprising a Riddick-type electrophoresis cell.

The use of a cationic polyelectrolyte flocculant, such as the Purifloc C 31 of Dow Chemicals, has given very satisfying results. Its application in the decontamination plant produced excellent and stable settling conditions which resulted in doubling the previously obtained process rates.

EUR 4401 e

EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

**ZETA POTENTIAL CONTROL APPLIED
TO THE TREATMENT OF RADIOACTIVE EFFLUENT**

by

A. J. GILLOT-STOKKINK and R. LOPES CARDOZO

1969



**Joint Nuclear Research Center
Ispra Establishment — Italy**

**Chemistry Department
Organic Chemistry**

ABSTRACT

The aim of the present study was the improvement of working conditions in the decontamination plant for radioactive effluent at Ispra. This plant operates by a scavenging-flocculation process. The generally applied but unprecise "beaker tests" used for sedimentation control were completed by precise measurements of the surface charge or zeta potential of the radioactive sludge suspensions. This allowed the exact choice of appropriate reactants and dose rates for optimum flocculation in the case of each type of effluent to be treated. Zeta potential measurements were performed with a commercialised device called "Zeta-meter", comprising a Riddick-type electrophoresis cell.

The use of a cationic polyelectrolyte flocculant, such as the Purifloc C 31 of Dow Chemicals, has given very satisfying results. Its application in the decontamination plant produced excellent and stable settling conditions which resulted in doubling the previously obtained process rates.

KEYWORDS

RADIOACTIVE WASTES
WASTE PROCESSING
DECONTAMINATION
FLOCCULATION
PRECIPITATION
SUSPENSIONS
CHEMICALS

<u>CONTENTS</u>	Page
1. Introduction	3
2. General aspects of the properties of colloidal suspensions	3
3. Zeta potential - Description and determination	5
3.1. Description of the zeta potential	5
3.2. The principles of flocculation of colloidal suspensions	6
3.3. Determination of the zeta potential	8
4. The flocculation process in practice	11
4.1. Mechanism of inorganic flocculants	11
4.2. Nature and mechanism of organic polyelectrolyte flocculants	12
4.3. Effects of pH variations on zeta potentials and flocculation	13
5. Experimental part	13
5.1. Experimental program	13
5.2. Equipment used	14
5.2.1. Zeta potential measurements	14
5.2.2. Measurements of the rate of sedimentation	16
5.2.3. pH measurement	17
5.3. Experimental data	17
5.4. Experimental results	17
6. Discussion	17
6.1. Zeta potentials of radioactive effluents before scavenging-coprecipitation	17
6.2. Zeta potentials after the scavenging-coprecipitation treatment	24
6.3. Zeta potential in function of flocculant addition	26
6.4. Zeta potential and sedimentation	27
7. Conclusions	28
Acknowledgement	28
Bibliography	29

ZETA POTENTIAL CONTROL APPLIED TO THE TREATMENT OF
RADIOACTIVE EFFLUENT*)

1. INTRODUCTION

The chemical decontamination of radioactive effluents of low and medium activity (10^{-6} to 10^{-2} $\mu\text{C/ml}$), as applied at the CCR Ispra**), is based on the extraction of the radioactive matter from the contaminated solution, achieved by the scavenging co-precipitation method, and on a complementary flocculation-clarification step, aiming at the rapid settling of sludge particles.

The whole process is performed in a so-called flocculator (see Fig. 1), and can be characterized by the following steps:

- Addition of the appropriate chemicals in zone 1 for the co-precipitation step, requiring for instance the following ions: Ca^{2+} , Fe^{2+} , Fe^{3+} , PO_4^{3-} ...
- Adjustment of the pH (around 11) by NaOH addition (zone 2).
- Formation of small aggregates by gentle stirring (in zone 3).
- Addition of flocculant (zone 4).
- Agitation followed by formation (in zone 5) of larger flocs which are carried upwards.
- Sedimentation (zone 6).
- The purified supernatant effluent leaves the flocculator by over-flow; the settled radioactive sludge is extracted from the bottom of the flocculator, concentrated by a centrifugal separator[2] and sent to appropriate treatment- and storage facilities.

In such a process, the settling rate of the chemical flocs and the stability of the sludge-blanket are important factors. Usually the control of the sedimentation rate is carried out by means of a "beaker" test which consists of a mere visual observation of particle (or turbidity) sedimentation in a static mass of water. Such a control does not supply sufficiently representative information, since an apparently well sedimenting mass of flocs might be unstable under the influence of turbulence and time.

The aim of the present study was to elaborate a more exact control method, based on the physico-chemical properties, mainly the measurement of the zeta potential, ZP, or surface charge of the colloidal particles in suspension, during the various stages of the decontamination process, but in particular in the flocculation stage. The influence of the polyelectrolyte coagulants on the decontamination rate itself is studied separately and will be subject of a future report.

2. GENERAL ASPECTS OF THE PROPERTIES OF COLLOIDAL SUSPENSIONS

The main problem in effluent decontamination is the identification and the measurement of all factors which may influence the sedimentation rates of the suspended impurities. This enables the appropriate choice of the nature and the concentration of reagents

*) Manuscript received on 3 September, 1969.

**) Described in detail elsewhere [1,2].

which may increase settling rates and consequently the output as well as the quality of the decontaminated effluents. Most of the usual processes are based on empirical data, such as the above mentioned beaker test. Blanco et al. [3] were among the first to apply zeta potential measurements to radioactive effluent treatment. However, during the last years this method has proved to be increasingly useful in tests of non-active waste waters from rivers or factories [4-11].

In effluents the suspended particles are generally of inorganic nature including finely divided silt-particles, small precipitates as well as an organic fraction derived from decomposed plant and microbe growths. In the case of radioactive effluents, the decontamination process by coprecipitation increases the number of suspended particles. Particle diameters may extend from normal floc dimensions (of 1 mm or more to 0.1 mm) down to the colloidal range ($1/\mu$ to $1\text{ m}/\mu$). This makes it obvious that:

- 1) Complete visual observation of such a large range of particle diameters is practically impossible, the visibility range of the eye being limited at 0.1 mm.
- 2) The sedimentation rates of so widely spread suspensions are extremely variable.

The sedimentation rate of the suspension may, in the first instance, be estimated by application of Stokes' law [4,12] which gives the sedimentation velocity of small spheres in a liquid medium:

$$v = \frac{g (\rho_1 - \rho_0) d^2}{18 \eta} \dots (1)$$

where:

v	=	velocity at steady fall	(cm/sec)
d	=	the particle diameter	(cm)
ρ_1	=	the density of the particle	(g/cm ³)
ρ_0	=	the liquid density	(g/cm ³)
η	=	the viscosity of the liquid	(poises)
g	=	the acceleration due to gravity	(980 cm/sec ²)

By applying Stokes' law to evaluate the theoretical sedimentation velocity of particles of a density of 2.7 g/cm³ in clear water (of viscosity = 0.01 poise), it follows that the settling velocity for current "coarse turbidity" of about 0.1 mm is 1.0 cm/sec. For the "upper colloidal range" from $1/\mu$ to $0.1/\mu$ the velocity is around 4 to 0.04 mm/hr and for the finest colloids of $1\text{ m}/\mu$, the velocity is only 0.04 mm/year.

In order to have sedimentation of the bulk of the colloidal matter in a reasonable span of time, it is necessary to induce agglomeration, which increases the mean particle diameter and hence the settling rate. However, agglomeration will be opposed by the electric charge (or zeta potential) on the surface of almost all suspensions, especially of lyophobic particles. These surface-

charges, due to the existence itself of the solid-liquid interfaces, are sometimes positive but generally negative. The mutual repulsion of such particles, especially if numerous, will counteract the agglomeration and can be responsible for the fact that the matter remains in suspension. It is noted that a normal settling process according to Stokes' law may also be upset in a dynamic regime by the presence of local turbulence and currents, as may occur during the flow through the flocculator. However, in practice, the flow regime is usually laminar.

The principle problem in the art of water decontamination remains the precise knowledge of the zeta potential of the suspended particles and of all factors that influence this potential. Only by knowing this potential it is possible to obtain optimum flocculation and convenient floc sedimentation.

3. ZETA POTENTIAL. DESCRIPTION AND DETERMINATION

3.1. Description of the zeta potential

A schematic representation of the concept of the zeta potential in the case of an electronegative particle in suspension in water is given in Figure 2 [6,12,13].

In nature, almost all raw-water colloids are electronegative, which means that they have an excess of negative ions at their outer surface or firmly adsorbed on this outer surface. The cause of the predominantly negative charge is tentatively explained [16] as being due to the preferential adsorption of the highly polarisable small sized OH^- (or other negative) ions, which fit better into the lattice of a colloid than the often larger positive cations. The greater affinity of the positive ions for water tends to exclude the less hydrated negative ions from the bulk of the liquid which are then accumulated at the liquid-solid interfaces.

Figure 2 shows how the first layer of firmly attached negative charges creates the presence of an opposite layer of positive counterions from the solution, drawn to the colloid by electrostatic attraction [4,15]. In the hypothetical case of absence of thermal agitation or Brownian movement, this layer of positive counterions will form a compact double layer or "Stern" layer, the number of the cations being in number equivalent to the negative charges on the surface (Fig. 3a). In this way the screening power of the larger cations will neutralise the field-effect from the negative surface, leaving undisturbed all the remaining ions in the bulk of the solution. In reality there always exists a thermal agitation or Brownian motion, with the effect that part of the counterions tend to be redistributed into the solution, remaining however within the field of attraction on the surface of the colloids. This forms the so-called "diffuse double layer" or Gouy-layer (see Fig. 2 and 3b), with a gradual drop of the potential from maximum (of the order of 100-150 mV) to zero at the limit of the undisturbed bulk of the solution. The total electric potential from the colloid surface to the limit of the diffuse layer is called the Nernst potential. In this case it is admitted that there still remains a layer of rigidly attached counterions (the Stern layer), but inferior in number, to the negative surface charges, the

remaining charges of counterions being distributed within the diffuse layer. The boundary between the immobile part of the double layer (or solvent layer adhering to the particle in its motion) and the diffuse layer within the solvent (which can move with respect to the particle) is called the hydrodynamic plane of shear. The potential drop between this plane (which essentially separates the water of hydration from the free water) and the limit of the diffuse layer, is called the zeta potential [12 to 15]. This potential is considered not to include the potential of the Stern layer, which anyhow has only a thickness of the order of a molecule, whereas the total diffuse layer corresponds to some 300-400 Å [15].

3.2. The principles of flocculation of colloidal suspensions

As both a small diameter and a high zeta potential (or a large double-layer), are responsible for the state of suspension of the colloidal matter, it is necessary to act upon these entities in order to transform a suspended stable sol into a mass of settling flocs, for instance by the addition of a simple electrolyte [15]. Assuming that there is no specific chemical reaction between the particle and the added electrolyte, the latter simply supplies counterions and simillions in the bulk of the solution which enter into the double layer thus modifying its structure.

It is specifically the nature and the valence of the counterions that are determinant; their additional presence decreases the thickness of the double layer, neutralises its charge and drops the potential. If the action of the counterions is limited to the range around the isoelectric point, the various colloidal particles will no more repel each other and mild agitation may cause contacts. This leads to particle agglomeration by the possible action of short range forces, such as Van der Waals forces, adsorption, cohesion and interlocking forces. The isoelectric point will be attained at a precise concentration of a simple electrolyte. This concentration is called "flocculation value". This value has to be established correctly, or otherwise for concentrations exceeding this value, the presence of the extra counterions will change the sign of the initial colloid, so the initially negatively charged particles might become positive with a renewed probability of particle repulsion, thus reproducing suspension.

The action of the added electrolytes on the zeta potential depends on the sign of the charge, the valency and the size of the added active ions [12,15]. Polyvalent ions are far more powerful than monovalent ions, whereas larger ions have less flocculating power. According to the Schulze-Hardy rule, bivalent ions of electrical charge contrary to the sign of the colloid, have 10 to 100 times more flocculating power than monovalent ions, whereas trivalent ions again have 10-100 times more power to flocculate than bivalent ions. On the other hand, the effect of the ion radius has been defined by the Hofmeister-series of cations and anions of decreasing flocculation power, corresponding to increasing radii of the (hydrated*) ions [12 to 16] (see Tables I, II and III).

*) In solutions it is the action of the hydrated ions that counts.

TABLE I

Hofmeister series [12,15].

<u>Cations of decreasing flocculation power</u>	
Ba ²⁺ > Sr ²⁺ > Ca ²⁺ > Zn ²⁺ > Mg ²⁺ » Rb ⁺ > K ⁺ > Na ⁺ > Li ⁺	
<u>Anions and negative radicals of decreasing flocculation power</u>	
F ⁻ > IO ₃ ⁻ > H ₂ PO ₄ ⁻ > BrO ₃ ⁻ > Cl ⁻ > ClO ₃ ⁻ > Br ⁻ > NO ₃ ⁻ > ClO ₄ ⁻ > I ⁻ > CNS ⁻ and citrate ³⁻ > tartrate ²⁻ > SO ₄ ²⁻ > C ₂ H ₃ O ₂ ⁻ > Cl ⁻	

TABLE II

Effect of ionic radius on flocculation values [16].

Salt added	Flocculating value mM/liter	Ionic radius (Å)	
		Hydrated*)	Crystal*)
Negatively charged AgI			
LiNO ₃	165	2.31	0.78
NaNO ₃	140	1.76	1.00
KNO ₃	136	1.19	1.33
RbNO ₃	126	1.13	1.48
Mg(NO ₃) ₂	2.60	3.32	0.75
Zn(NO ₃) ₂	2.50	3.26	0.83
Ca(NO ₃) ₂	2.40	3.00	1.05
Sr(NO ₃) ₂	2.38	3.00	1.20
Ba(NO ₃) ₂	2.26	2.78	1.38
Positively charged Fe ₂ O ₃			
KCl	9.0	1.17	1.80
KBr	12.5	1.15	1.96
KI	16	1.16	2.20

*) Note: hydrated-ion radii increase in inverse order with respect to crystal-ion radii.

TABLE III

Flocculation values of some simple electrolytes [16].

Negatively charged As_2S_3			Positively charged Fe_2O_3		
Salt added	Millimoles per liter	Relative conc.	Salt added	Millimoles per liter	Relative conc.
NaCl	51	100	NaCl	9.25	100
KCl	49.5	97	KCl	9.0	97
KNO ₃	50	98	$\frac{1}{2}BaCl_2$	9.6	104
$\frac{1}{2}K_2SO_4$	65.5	128	KNO ₃	12	130
LiCl	58	107			
MgCl ₂	0.72	1.41	K ₂ SO ₄	0.205	2.22
MgSO ₄	0.81	1.55	K ₂ Cr ₂ O ₇	0.195	2.12
CaCl ₂	0.65	1.28	Ti ₂ SO ₄	0.22	2.38
ZnCl ₂	0.68	1.32			
AlCl ₃	0.093	0.182			
Al(NO ₃) ₃	0.095	0.186			
Ce(NO ₃) ₃	0.080	0.156			

3.3. Determination of the zeta potential

In order to give a simplified but sufficiently exact formulation of the zeta potential of a particle suspended in a liquid medium, in first approximation the most frequent case is considered where the double layer is much smaller than the curvature of the particle (see Fig. 2 and 3c). The zeta potential is then reduced to the so-called "Helmholtz-layer". This layer is considered as a condenser with equal opposite charges, separated by the double layer thickness δ . The charges are given by the area times the charge density q . Denoting D as the dielectric constant of the intervening medium, the zeta potential, ZP , is given by [15]:

$$(ZP) = 4\pi q \delta / D \quad \dots (2)$$

Experimentally the measurement of the zeta potential has been made possible by use of the so-called electrophoresis cell, in which the charged particles, suspended in a non-conducting medium, move in an electric field. Such a cell (Figure 4) is essentially a tube of small diameter, with an electrode at each extremity. When a potential difference V is applied along the cell length L , the colloidal particles suspended in a liquid medium of viscosity η , move with a velocity v towards the electrode of sign opposite to that of the surface charge q . In such a case, the velocity v will be proportional to the charge, the double layer

thickness δ and the potential difference V , but inversely proportional to the tube length L and the viscosity. Thus,

$$v = q. \delta . V / L . \eta \quad \dots (3)$$

As Equation (2) gives

$$q. \delta = (ZP). D / 4 \pi \quad \dots (4)$$

Equation (3) becomes

$$v = (ZP). (D / 4 \pi). (V / L \eta) \quad \dots (5)$$

Denoting

$$V / L = V' \quad \dots (6)$$

the voltage drop per unit length (cm), the mobility μ or particle velocity per voltage drop per cm becomes

$$\mu = v / V' \quad \dots (7)$$

From Equations (5) and (7) it follows that

$$\mu = (ZP). D / 4 \pi \eta \quad \dots (8)$$

or

$$(ZP) = \mu (4 \pi \eta / D) \quad \dots (9)$$

This is the simplified Helmholtz-Smoluchovsky formule for the determination of the zeta potential by means of an electrophoresis cell. In Equation (9):

- (ZP) = the zeta potential in e.s.u.
- μ = the particle mobility in cm/sec per e.s.u./cm
- η = the viscosity of the liquid in poise at the given temperature
- D = the dielectric constant of the liquid at the given temperature.

In practice, Equation (9) becomes [17]

$$(ZP)_T = 113,000 \times \mu \cdot \eta_T / D_T \quad \dots (10)$$

where

- $(ZP)_T$ = the zeta potential calculated in millivolts at temperature T
- μ = the mobility in microns/cm per volt/cm
- η_T = the viscosity at temperature T
- D_T = the dielectric constant at temperature T.

According to Equation (10), the determination of the zeta potential is reduced to the measurement of the mobility of the colloids of a given solution. In practice, with an apparatus such as the Zeta Meter (see Chapter 5.2.), colloid displacement is observed in the electrophoresis cell by means of a stereoscopic microscope,* and the measurement of the mobility is reduced to a simple observation of the time of displacement of the particle between 2 marks of known distance on a fixed scale in the microscope, at a known potential. This gives directly v and thus μ (see Equation (7)) and the zeta potential by means of Equation (10). Making use of already plotted charts delivered by the Zeta Meter Cy. [17] the ZP value can be read directly corresponding to each time of displacement at a given temperature.

As indicated above, the formula of Helmholtz-Smoluchowsky gives a first approximation of the zeta potential of particles with a small double layer with respect to the particle radius (the particle being non-conductive). When the thickness of the double layer is much larger than the particle radius, the Hückel Equation has to be used:

$$(ZP) = \mu \cdot (6\pi\eta/D) \quad \dots (11)$$

But in general, the first formula covers most practical needs [17]. It covers the observation visibility of particles in an electrophoresis cell ranging mostly from 10^2 to 10^5 Å in solutions with normalities varying from 1 to 10^{-5} .

Experimentally it is found that a given colloidal solution yields not one particular value of zeta potential, but a characteristic Maxwellian-like spread around the average value. This spread is due to slightly variable constitutions of the double layer. Examples of zeta potential distribution curves are given in Figure 5. Average zeta potential values of raw water colloids lay generally in the range of -16 to -22 mV (+ 6 to + 20 mV) [5,7]. It seems that the largest spread corresponds to the most contaminated effluents.

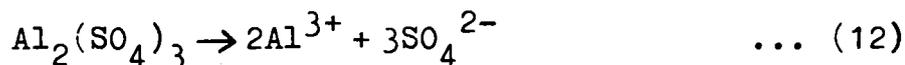
*) With special dark field illumination.

4. THE FLOCCULATION PROCESS IN PRACTICE

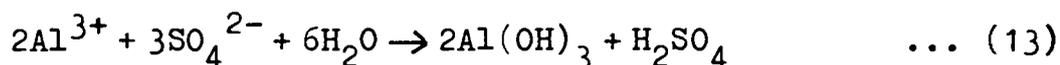
Considering the large spread in zeta potential values of one particular suspension, it seems almost impossible that a single coagulation treatment might bring the charge of each and every colloid to zero, as would be required for optimum flocculation conditions. On the other hand, if a treatment simply adds a given positive potential to all particles, this would only lead to a displacement of the distribution curve with the maximum or the average value corresponding to 0 mV, but with overlapping values spreading on both sides. However, Abramson and Riddick [7] showed that it is possible to reduce every single colloid to zero zeta potential. This can for instance be obtained by the use of inorganic flocculants such as aluminum sulphate (alum) or iron salts. Flocculants such as organic polyelectrolytes of various chain lengths and of positive, neutral or negative excess charges are equally applied successfully.

4.1. Mechanism of inorganic flocculants

The efficiency of certain specific inorganic flocculants is explained by the action of the multivalent ions such as Al^{3+} or Fe^{3+} according to the Schulze-Hardy law given above. For instance, when aluminum sulphate is added to the effluent to be treated, it first dissociates as



The Al^{3+} ion is immediately attracted to and absorbed on the colloid. Then directly hydrolysis occurs according to



As a result the colloid is coated with a uniform layer of aluminum hydroxide or hydrous aluminum oxide ($Al_2O_3 \cdot nH_2O$). As this layer masks all charges, the zeta potential is dropped to zero on all colloidal particles. The immediate formation of these hydrated oxides, within seconds, can be observed by a pH drop and by the opalescence due to gel formation. The gel consists of aligned polymer-like elements which build up around the colloids, if available. But if no colloids are in their immediate neighbourhood, these "polymers" undergo autogeneous build-up and floc formation.

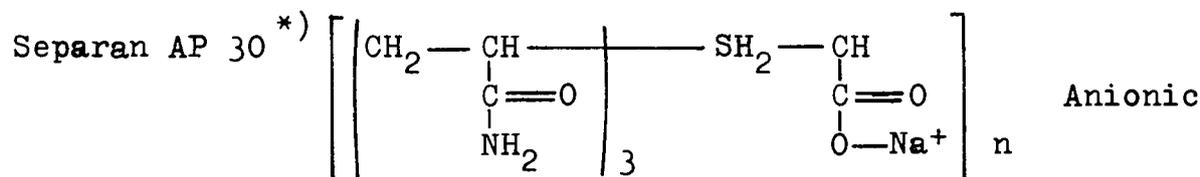
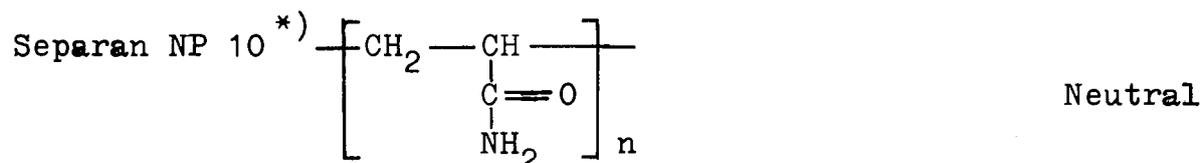
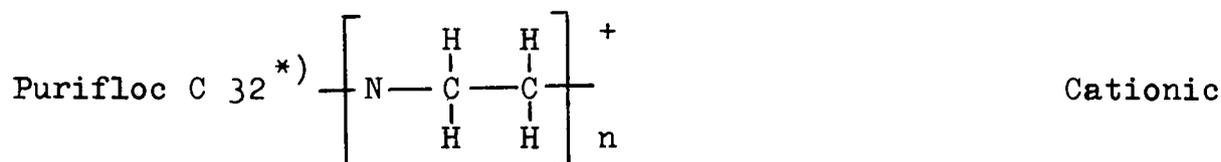
In practice, only violent stirring at the introduction of alum in the contaminated water allows sufficiently rapid contact probabilities with the resulting colloid coating. In that case, any colloid, e.g. from -10 to -60 mV, will be coated with a similar absorbed hydrous aluminum oxide layer, bringing the zeta potential uniformly to 0 mV at proper salt-concentrations.

The once formed hydrous aluminum oxide aggregates are very light and fragile due to their low degree of aggregation and lack of adequate chemical interlocking. In practice the resulting floc

should be tough and tenacious. This is often achieved by the addition of activated silica. However, this increases the amount of neutralizer needed as the silica potential in solution is around -15 mV. In order to "toughen up" the flocs, a short to medium chain cationic polyelectrolyte can be used after alum treatment. When the final zeta potential value has reached the 0 to +5 mV range, a high molecular long chain non-ionic or anionic organic polyelectrolyte may be added for final floc gathering and sedimentation.

4.2. Nature and mechanism of organic polyelectrolyte flocculants

Organic flocculants are high molecular polymers mostly of a medium to long chain-structure, bearing active sites which are either predominantly cationic or anionic but can also be neutral. Some examples of the polymeric structure where molecular weights of over 10^6 can be encountered, are:



The active sites assure the adsorption of colloids of the opposite sign, thus tending to neutralize the total initial charge. On the other hand the chain structure produces a bridging action amongst the various adsorbed colloids, thus agglomerating them to great and heavy flocs which settle rapidly.

Even in the case of neutral polyelectrolytes there always seem to remain some active sites allowing particle adsorption. Moreover, the long chain apparently closes on itself, rapidly imprisoning the present colloids. In all cases proper agitation should be applied according to manufacturers instructions, in order to bring colloids and flocculants into close contact, otherwise chain bridging and sedimentation of flocs might occur without colloid gathering. If colloid potentials and optimum flocculant concentrations are not properly predetermined by zeta potential measurements, erroneous treatment may easily result. For instance, an excess cationic polyelectrolyte may reverse the initially negative sign of the zeta potential of the colloids. Although sedimentation rates for slight excesses of flocculant generally seem to

^{*)} Furnished by Dow Chemicals.

vary little around the 0 mV range (through simultaneous action of floc weight and charge increase), the flocs acquire a tendency to become instable because of accumulation of excessive positive charges, which may tend to redisperse the colloids as soon as local currents or agitation breaks the agglomerates. Similarly, when an anionic or neutral polyelectrolyte is (erroneously) applied directly to a initially negative colloid, the presence of a few active sites (generally available) will suffice to produce some primary adsorption and together with the bridging action large flocs will be formed. This results in an apparently good flocculation, but the slightest current or agitation may break these flocs and redisperse the still more charged colloids. Various types of polyelectrolytes are presently on the market, often tailor-made for special purposes. The manufacturers usually prescribe the optimal way to introduce the coagulant into the solution, indicating mixing velocity, mixing time, optimal pH range etc ... Examples of typical applications of various flocculants [4] are given in Figure 6.

4.3. Effects of pH variations on zeta potentials and flocculation

As shown in the literature [7], pH variations resulting from additions of bases or acids to colloidal solutions may lead to zeta potential variations in certain specific regions which vary from case to case.

In the example of Figure 7a, the zeta potential is seen to be independent of the pH in the middle pH range, but varies between pH 9 to 12, or below pH 6 (after additions of 0.1 NaOH, or 0.1 N HCl). In the lower part of the pH scale, the H^+ counterions play a predominant role and decrease the negative zeta potential layer. After an addition of NaOH, first the effects of both ions seem to outbalance each other. After pH = 9 the highly polarisable OH^- ions seem to increase the negative charge whereas at the highest concentrations only the Na^+ ions of low flocculation power act as counterions. In any case it is important to control the effects of initial pH on the zeta potential for each effluent treatment and on the flocculation values for each flocculant applied, especially at the upper limit of the pH scale. Figure 7b shows how the addition of HNO_3 , at initial pH = 12, increases further the already positive zeta potential.

5. EXPERIMENTAL PART

5.1. Experimental program

The experimental study consisted principally of measurements of the zeta potential, or surface charge, of the colloidal particles contained in the radioactive effluents. The measurements were made before and during the effluent treatment, according to the method described in Chapter 1. Thus the zeta potentials were measured on the initial effluents, directly after introduction of the chemical reagents (for scavenging-precipitation of the radioactive ions) to determine the sign and amplitude of the charge before flocculant addition and finally after addition of various amounts of flocculant.

This made it possible to trace the zeta potential/flocculant-concentration graphs in order to find the concentration at zeta potential equal to zero mV, the isoelectric point which corresponds to optimum sedimentation conditions. For comparison some supplementary measurements were made on non-active solutions.

In relation to zeta potential controls the following secondary measurements were made:

- pH control of each solution, as well as some tests of the pH-zeta potential relation.
- The sedimentation velocity was measured as a function of flocculant concentration and then the resulting correlation between zeta potential and sedimentation velocity was considered at given flocculant doses. Sedimentation control was performed using a classical method, a variant of the beaker-test. The entity measured was the time necessary to reduce the suspended sludge-blanket volume to one-half by sedimentation, as observed in a graduate cylinder after initial mixing.
- In some experiments, the sedimentation velocity was measured by turbidity control, the measured entity being the time necessary to reduce to one-half the "turbidity" at a certain level in a transparent rectangular vessel after initial mixing.
- The aging effect of the solutions was also considered up to a certain point, by intercorrelating zeta potential as well as pH alterations with time, considering solutions which were measured after one day to about one month.
- The influence of additions of KMnO_4 (at concentrations used for de-emulsification of certain solutions) on zeta potential values was also examined in a few particular cases.

5.2. Equipment used

5.2.1. Zeta potential measurements

For the measurement of the zeta potentials of the colloidal particles in the solutions to be examined, the "Zeta Meter"*) was used. This apparatus is composed essentially of:

- a Riddick-type electrophoresis cell;
- a stereoscopic microscope with special dark-field illumination, which enables measurements on particles down to the 0.1 micron range;
- a power unit with incorporated voltmeter, amperemeter and a timer. The latter has a numerical counter for the tracking of the colloids.

As explained in Chapter 3.3., the measurement of the time necessary for an observed particle to cover a known path under the influence of a given electric field (potential drop per cm = V'), leads to the knowledge of the particle velocity v, its mobility $\mu = v/V'$ and the zeta potential:

*) By Zeta Meter Cy., 1720 First Avenue, New York. Represented in Italy by Carlo Erba, via Imbonati 24, Milano. For the mode of use, reference is made to the instructions of the manufacturer [17].

$$(ZP)_T = 113,000 \cdot \eta_T / D_T \quad \dots (10)$$

for a solution of viscosity η_T and dielectric constant D_T at temperature T. For water solutions at 20°C, $\eta_T \approx 0.01$ poise and $D_T = 8.36$. Thus Equation (10) becomes at 20°C $\eta_T \approx 0.01$:

$$(ZP)_{20^\circ} = 13.5 / \mu \quad \dots (14)$$

Normally mobility measurements in an electrophoresis cell include a factor due to electro-endosmosis, this is the relative movement of the charged particles in the solution with respect to the charged interface at the wall of the cell. The Zetameter gives special viewing facilities to operate directly on the zero-endosmosis level. Thus formulas (10) and (14) represent pure zeta potential mobilities.

As zeta potential values are dependent on temperature, it is preferable to operate at constant temperature, for instance 22.5°C. Moreover it is advisable to check regularly the conductance of the solution, as a relatively high conductance, (in practice above 3000 - 4000 micromhos/cm) produces rapid temperature increase in the cell and finally thermal overturn with gas-release at the electrodes. This would lead to false readings and thus limit the correct operating time δ . The specific conductance is directly determined with the Zetameter:

$$\delta = K I / V \quad \dots (15)$$

where V and I are cell voltage and current, given directly by readings on the incorporated volt- and ammeter, whereas K is the cell constant (around 70.5) determined once and for all with a known solution. It follows that δ can be directly read from the ammeter when taking V = 70.5 Volts. δ

Since the actual zeta potential values of each colloidal solution show a Gaussian-like distribution, it is necessary to take at least 10 to 30 readings for each sample renewing the sample 2 to 3 times to avoid experimental errors and then deduce the average zeta potential. The tracing of the distribution curves requires the counting of 50 to 100 particles. In general the determination of only one distribution curve is sufficient for each new type of solution examined. The precision of the final zeta

*) The Zeta Meter Cy. charts [17] allow direct readings of zeta potential as a function of t, T and V.

**) Another Zetameter chart directly gives time limits of measurement before thermal overturn at each particular conductance and applied voltage, enabling the choice of the best voltage.

***) In the following reported experiments, $\delta = 700$ micromhos/cm for the standard solutions and $\delta = 2000-4000$ micromhos/cm for radioactive effluents if a molybdenum anode is used.

potential measurements reported here, is of the order of $\pm 15\%$. The precision can of course be increased by increasing the number of readings.

Time measurements have a precision of ± 0.2 sec. The microscope scale readings are taken $\pm 3\mu$ (on a 30μ scale). Voltage readings are ± 2 volts. Temperature readings are $\pm 0.25^\circ\text{C}$. Although the most frequent standard deviation of the zeta potential determined was around ± 3 mV, the total spread of the zeta potential values for each colloid in a given solution may vary from some 12 to 45 mV.

The precision of the measurements around zeta potential = 0 mV is worst, as measurements are very difficult on rapid settling flocs. In such a case the solution must be either often replaced or flocs resuspended by a special technique. In practice it is advisable to avoid such measurements and take readings at flocculant concentrations somewhat above and somewhat below the probable flocculation value at zeta potential = 0 (at least ± 5 mV), since the zeta potential/flocculant concentration relation is practically linear in the zero potential range (see Chapter 6).

5.2.2. Measurements of the rate of sedimentation

The sedimentation of the particles in suspension in the examined solutions, was determined by using a simple graduated transparent cylinder of 100 cc and ca 25 mm diameter. After initial homogeneous mixing, the solution was poured into the tapped cylinder and again mixed before starting observations. First the sedimentation curve (V, t) was traced, V being the volume of sludge particles in sedimentation at the time t . This volume was defined by visual observation of the lowering upper interface-level between the clear supernatant solution and the total volume of particles remaining in suspension (or already sedimented). In fact, this level is well defined only when the diameters of the particles have a discrete value. It hardly exists if particle diameters vary widely from very fine to coarse [15]. In the latter case, (gradual sedimentation) only the level presenting the greatest discontinuity is noted. In some other cases, "inversed sedimentation", no clear upper boundary was observed but the rising level of the "lower boundary" was noted: in reality this is the interface between sedimented and non-sedimented particles. The time necessary to reduce to one half the initial volume of suspended particles (or $t_{V\frac{1}{2}}$) is the most representative value of the sedimentation rate.

Sedimentation rates were also controlled by measurements of the turbidity using the "Trübungs-Messer" (Nr. 2800) of Dr. B. Lange of Berlin. In this small apparatus, the turbid solutions to be measured were poured into rectangular transparent plastic vessels of 100 cc and placed between a light source and a selenium photoelement. The moment the cell was filled, was taken as time $t = 0$ and the clearing up of the turbidity was recorded as a function of time by simple transmission measurements: maximum light-transmission corresponded to zero turbidity, whereas zero transmission or maximum turbidity corresponded to 100 arbitrary units. The sedimentation rate was represented by the so-called "turbidity half-time" or time necessary to reduce to one half the initial turbidity.

Time measurements were recorded with a precision of ± 0.5 second. The precision of the sedimentation volume was at best ± 1 to ± 3 cm³ or more in case of irregular sedimentation. The turbidity factor was read with a precision of ± 1 unit*).

5.2.3. pH measurement

pH measurements were performed with a standard type pH-meter, type 390 pH of WTW**) using a glass electrode. Precision of the measurements was ± 0.05 pH.

5.3. Experimental data

Specific data concerning the solutions examined, the chemicals added for scavenging-precipitation and the flocculants used to study coagulation-sedimentation, are given in the Tables IV to VII.

5.4. Experimental results

The principal numerical results of the experiments are given in Table VIII.

Examples of the relations between zeta potential and various parameters such as flocculant nature and concentration, turbidity, sedimentation rate, pH etc ... are shown in a series of graphs (Figures 8 to 17).

6. DISCUSSION

6.1. Zeta potentials of radioactive effluents before scavenging-coprecipitation

The zeta potentials of the untreated effluents were examined in the case of a few solutions only (see Table IX).

TABLE IX

Zeta potentials of some untreated radioactive effluents.

Sol. No	ZP (mV)	Initial concentration (ppm)	
		Ca ²⁺ + Mg ²⁺	PO ₄ ³⁻
h	-14.2	60	98
e	-10.2 to -8.4	81	36
f	-6.3	121	23

*) Experience showed that in the present work the sedimentation cylinders gave more representative results than the turbidity cell.

**) Wissenschaftlich Technische Werkstätten GmbH Weilheim OBB, Germany.

TABLE IV

Initial composition*) of solutions examined.

Solution No	Origin	Composition (ppm)				Initial pH	Radioactivity 10^{-5} $\mu\text{C}/\text{ml}$	
		$\text{Ca}^{2+} + \text{Mg}^{2+}$	PO_4^{3-}	Dry residue	Materials in suspension			
a	Distilled water	-	-	-	-	-	0	0
b	Tap water	20	-	-	-	-	0	0
c	Radioactive effluent	116	47	1375	34	6.5	-	-
d	" "	44	19	715	990	8	5.2	2.8
e	" "	81	36	1515	43	4.5	32.0	40.1
f	" "	121	23	2130	730	5.6	41.0	134.5
g	" "	28	6	545	260	6.5	2.7	4.4
h	" "	60	98	1120	290	6.4	7.8	5.2

TABLE V

Reagents added for scavenging-precipitation, values in ppm.

Treatment No	Ca^{2+}	$\text{Fe}^{2+} + \text{Fe}^{3+}$	Cu^{2+}	PO_4^{3-}	$\text{Fe}(\text{CN})_6^{4-}$	MnO_4^-	pH
1	50	16	25	80	40	-	10
2	100	100	-	30	-	-	11
3	80	80	-	200	-	30	11
4	100	100	-	50	-	-	11
5	120	120	-	60	-	55	11
6	140	140	-	60	-	55	11
7	100	100	-	50	-	55	11
8	100	100	-	50	-	25	11
9	100	100	-	50	-	-	12
10	60	100	-	50	-	30	10
11	100	100	-	50	-	30	10
12	13	30	-	120	-	-	11
13	30	30	-	120	-	-	11

*) As far as analysed.

TABLE VI

Chemical contents of the solutions before flocculant addition as resulting from addition of data in Tables IV and V.

Solutions before flocculation	Ca ²⁺ + Mg ²⁺	Fe ²⁺ + Fe ³⁺	PO ₄ ³⁻	Cu ²⁺	Fe(CN) ₆ ⁴⁻	MnO ₄ ⁻
a 1	50	16	80	25	40	-
a 2	100	100	30	-	-	-
a 13	30	30	120	-	-	-
b 12	33	30	120	-	-	-
c 1	166	16	127	25	40	-
c 2	216	100	77	-	-	-
d 3	124	80	219	-	-	30
e 5	200	120	96	-	-	55
e 6	220	140	96	-	-	55
f 6	260	140	83	-	-	55
f 7	220	100	73	-	-	55
g 8	128	100	56	-	-	25
h 9	160	100	148	-	-	-
h 10	120	100	148	-	-	30
h 11	160	100	148	-	-	30

TABLE VII

Organic polyelectrolyte flocculants used.

Symbol used	Commercial name	Nature of flocculant	Manufacturer
C 31	Purifloc C 31	Cationic	Dow Chemicals
N 17	Purifloc N 17	Non-ionic	Dow Chemicals
A 2900	Praestol 2900	Anionic	Stockhaus & C
N 2700	Praestol 2700	Non-ionic	Stockhaus & C

TABLE VIII

Experimental Results

Zeta potentials, turbidity and sedimentation rates of colloidal suspensions in standard solutions (a,b) and radioactive effluents (c to h) as a function of cationic (C), anionic (A) and non-ionic (N) organic polyelectrolyte flocculants.

No Solution or Effluent	Flocculant		Zeta Potential (mV)	Turbidity Half-time $t_{\tau \frac{1}{2}}$ (min)	Sedimenta- tion Half-time $t_{v \frac{1}{2}}$ (min)	Initial pH	Final pH	Remarks	Age (days)	
	Symbol	Concen- tration (ppm)							Initial Solution	Flocc. Addition
a 1	C 31	0	-27	3.7	-	10	8.9	Breaking point	27	-
		60*	0	6.1	-	10	-		-	-
		80	+ 3.4	6.7	-	10	8.2		28	0
		200	+ 4.0	12.5	-	10	9.0		29	0
a 2	C 31	0	-16.6	4.0	-	11	10.6	Breaking point	1	-
		44*	0	1.7	-	11	-		-	-
		75	+ 9.8	1.5	-	11	10.7		3	0
		100	+ 9.8	1.2	-	11	10.4		9	0
a 13	C 31	0	-19.0	-	-	11	11.0	Breaking point	-	-
		20*	0	-	-	11	-		-	-
		30	+ 8.0	-	-	11	11.0		-	-
		50	+ 8.2	-	-	11	11.0		-	-
b 12	A 2900	0	-26.0	-	-	11	11		0	0
		1	-41.0	-	-	11	11		0	0
b 12	N 2700	1	-43.0	-	-	11	11		0	0
b 12	C 31	0	-18.0	-	-	11	11.0		30	30
		63*	0	-	-	11	-		-	-
		100	+10.5	-	-	11	11.0		30	30
c 1	C 31	0	-27	3.7	-	10	8.9	Breaking point	17	-
		51*	0	1.8	-	10	-		-	-
		80	+15.6	1.6*	-	10	8.2		23	0
		175	+17.3	0.8	-	10	-		21	0

TABLE VIII
Continuation.

No.	Flocc.	C	ZP	$t_{\frac{1}{2}}$	$t_{v\frac{1}{2}}$	pH _o	pH _f	Remarks	Age init.	Age fl.add.
c 2	C 31	0	-15.5	3.7	-	11	9.8-7.7	Breaking point	31-41	-
		36*	0	1.3	-	11	-		-	
		75*	+22.0*	0.7*	-	11	-		-	
		115	+25.0	0.5	-	11	7.6		42	0
d 3	A 2900	0.5	-29.5	3.75	-	11	-	Direct from plant	-	-
		0.9	-35.0	1.1	-	11	-	Lab. addit.	-	-
		1.5	-39.2	0.55	-	11	-	" "	-	-
		2.5	-38	0.5	-	11	-	" "	-	-
e 5	A 2900	0	-15.0	-	10**	11	11	Inversed sedimentation	3	0
		0.5	-17.8	-	3.15**	11	10	Normal sedimentation	7	0
		1.0	-18.2	-	2.45**	11	10	" "	7	0
		1.6	-20.0	-	2.25**	11	10	" "	4	0
		1.6	-19.0	-	-	11	9.6	" "	11	0
e 5	A 2900 + N 17	1.6 + 0.5	-18.8	-	2.10**	11	10.4	" "	4	0
		1.6 + 2.0	-18.0	-	-	11	-	" "	11	0
e 5	A 2900	2	-18.0	-	1.6	11	8.8		22	0
		5	-19.15	-	1.2	11	8.8		22	0
e 5	N 17	0	-15.1	-	6.8	11	10.4		10	10
		0.5	-16.1	-	6.0	11	10.4		8	0
		2.0	-17.1	-	5.0	11	9.8		8	0
		5.0	-16.0	-	4.1	11	10.7		8	0
e 5	N 2700	0	-11.6	-	8.3	11	10.7	Inversed sedimentation	4	4
		1	-11.5	-	6.7	11	10.8		4	0
		2	-11.6	-	6.75	11	10.8		4	0
		5	-17.9	-	10	11	11		5	0

TABLE VIII
Continuation.

2
:

No.	Flocc.	C	ZP	$t_{\tau \frac{1}{2}}$	$t_{v \frac{1}{2}}$	pH ₀	pH _f	Remarks	Age init.	Age fl.add.
e 5	C 31	0	-13.2	-	7.3	11	11		5	5
		300*	0	-	2.1*	11	-		-	
		600	-16.8	-	2.8	11	9.4		5	0
e 6	A 2900 + N 17	1.6 + 0.5	-11.0	35	7.0	11	11	Direct from plant-2 floc- culators in series	1	1
		1.6 + 1.5	-13.4	-	6.3	11	11		1	1
f 6	C 31	0	-10.4	-	7.0	10.6	10.6		7	-
		120*	0	-	3.5*	10.6	-		-	
		250	-	-	2.8	10.6	7.8		34	0
		300	+10.2	-	1.9	10.6	7.9		34	0
f 7	A 2900	0	-13.5	-	5.4	11	10.8		10	-
		2	-17.0	-	5.3	11	10		5	5
f 7	A 2900 + N 17	2 + 1	-16.8	-	5.75	11	-		5	0
		2 + 5	-17.9	-	6.7	11	10		5	0
f 7	A 2700 + N 17	2 + 0	-17.0	-	4.2	11	9.4		7	7
		2 + 2	-16.8	-	4.25	11	9.4		7	0
		2 + 5	-16.5	-	4.1	11	9.4		7	0
f 7	C 31	0	-13.5	-	5.4	11	10.8		10	0
		125*	0	-	2.6*	11	-		-	
		250	+14.6	-	1.3	11	-		27	0
		300	+12.3	-	1.0*	11	-		4	4
g 8	N 2700	2	-	-	3.75-5.8	11.0	11.0	Direct from plant	0 - 1	0 - 1

TABLE VIII
Continuation.

No.	Flocc.	C	ZP	$t_z \frac{1}{2}$	$t_v \frac{1}{2}$	pH ₀	pH _f	Remarks	Age init.	Age fl.add.
h 9	C 31	0	-13.9	-	2.8	12.1	12.1		0	0
		390*	0	-	1.9	12.1	-		-	-
		500	+ 7.6	-	1.7	12.1	12.0		1	0
		600	+ 8.85	-	1.8	12.1	12.0		2	0
h 9	N 2700	2	-19.6	-	1.3-1.7	12.1	12.0		0-2	0-2
		5	-22.9	-	0.9-1.8	12.1	12.0		0-12	0-12
h 9	N 17	3.5	-23.3	-	1.5	12.1	12.0	Sedimentation inversed after aging	0-12	0-12
		7	-19.8	-	1.1	12.1	12.0		0-2	0-2
h 10	C 31	0	-14.85	-	5.5	10.1	10.1	Breaking point	0	-
		80*	0	-	1.2*	10.1	-		-	-
		125	+ 8.8	-	0.9	10.1	9.7		4	0
		150*	+14.0*	-	-	10.1	-		-	-
		500	+13.7	-	1.2	10.1	9.7		0	0
h 10	N 2700	2	-17.2	-	0.45-	11.2	11-9.8	Direct from plant	4-9	4-9
h 11	C 31	0	- 9.1 to 12.1	-	4.0	10	9.7-8.1	Inversed sedi- mentation	0-11	-
		100*	0	-	1.3*	10	-		-	-
		225	+14.4	-	1.0	10	9.1	Breaking point	2	0
		500	+18.6	-	1.0	10	9.3		0	0

*) Graphically interpolated values.

**) Using graduated cylinders of 50 cm³ instead of 100 cm³.

For the examined solutions, the initial zeta potential values range from -6.3 to -14.2 mV, the total number of observable particles being however very low.

That the zeta potential values are negative was to be expected (see Chapter 3.1.), but they are nearer to 0 mV than data found in literature for normal effluent suspensions; these range generally from -15 to -25 mV [4,5,7,10,11]. This might be due to emulsifiers in the effluents, emanating from the radioactive laundry department.

When comparing the measured zeta potential values with the ion-content of the solutions (as far as analysed), it is notable that values tend towards 0 mV with increasing cation concentration and decreasing anion concentration. This is consistent with theory, as the cations become counterions to the negative particles, thus decreasing the double layer thickness. Reduction to 0 mV zeta potential requires an excess of counterions over simillions [16], an excess of anions will increase the negative double layer.

6.2. Zeta potentials after the scavenging-coprecipitation treatment

The zeta potentials of the particles in suspension in the effluents after the addition of the reactants for scavenging-coprecipitation are presented in Table X.

TABLE X

Zeta potentials after scavenging-precipitation, before flocculant addition.

Solution N°	Zeta potential (mV)
a 1	-27.0
a 2	-16.6
a 13	-19.0
b 12	-26.0
c 1	-27.0
c 2	-15.5
e 5	-11.6 to 15.1
f 6	-10.4
f 7	-13.5
h 9	-13.9
h 10	-14.9
h 11	-12.1

Zeta potential values measured here were between -10.4 and -27 mV, thus remaining more or less in the range of normal effluents as mentioned in literature (see Chapter 6.1.) before flocculant addition.

However, these zeta potentials are more negative than the values observed before this reaction. As is known, the aim was to form the precipitates which carry off the radioactive ions by adsorption and coprecipitation. Now it has to be considered that, although chemically neutral, these precipitates have a newly formed solid-liquid interface with the creation of a corresponding electric double layer. The value of the corresponding potential should depend on the nature of the free ions remaining in solution and their valencies, the OH^- content (see Fig. 7) and most probably the mode of formation of the particles. In this work, all data are not known, as all ions were not analysed and only the principal reactants are indicated. However, the present experimental results seem to confirm that the lower the content in cations and the higher the concentration in anions, which enter into the coprecipitation reaction, the more negative is the zeta potential of the formed precipitate. In fact, according to Mysel [15] the charges in the outer layer of a newly formed precipitate vary according to the relative concentrations of added cations or anions. Thus an excess of anions (here PO_4^{3-}) may produce a precipitate with an excess of negative charges in its outer layer; an excess of cations may reverse this charge considering also the effects of valency and ion diameter according to the Schulze-Hardy rule and Hofmeister series.

When presently considering the action of an electrolyte on already existing particles in solution, it is shown clearly [18] how zeta potential variations are determined by the action of the ion of highest valency. Thus initially highly negative zeta potentials are decreased by the additions of an electrolyte containing for instance tri- or bi-valent cations and mono-valent anions (AlCl_3 - CaCl_2), whereas negative charges are increased when electrolytes with multi-valent anions and mono-valent cations are added (K_2SO_4 - $\text{Na}_4\text{P}_2\text{O}_7$). In this work, the chemicals used were $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$.

Returning to Table X, it can be observed that the solutions a 1, c 1; b 12 with the highest negative potentials, correspond equally to relatively high doses in multi-valent anions and relatively low doses in cations. The fact that solution a 12 was only at a zeta potential of -19 mV may be due to the aging of the solution with the general effect of zeta potential values tending towards zero.

Solutions e and f had relatively high cation doses and low anions doses and zeta potential values range from -10.4 to -15.1 mV. Solution h seems to present a special case: zeta potentials remain more or less as they were before scavenging-precipitation. It may be assumed that the overall effects of cation and ion additions outbalanced each other in this case. Solution d, not measured at zero flocculant dosage had a very negative zeta potential value (circa -40 mV); the corresponding PO_4^{3-} dosage was particularly high (200 ppm).

In summary, these observations mean that the reactants for scavenging-precipitation might be chosen in a way as to keep the overall negative charge as low as possible. For this purpose reactants at minimum concentrations in polyvalent anions and maximum concentrations in polyvalent cations should be used.

This would reduce high negative zeta potential values, thus necessitating a lower flocculant dose to be applied afterwards.

Literature shows how increased lime additions on treated industrial effluents decreased zeta potentials from the -8 to -12 mV to the -7 to +5 mV range [11].

It is evident that the pH influence has to be taken equally into account since a low pH may reduce the double-layer thickness.

6.3. Zeta potential in function of flocculant addition

Consideration of experimental results as represented in Table VIII and in typical graphs such as Figures 8, 9, 12, 13 leads to the following observations:

- 1) Radioactive effluents, as analysed here, have negatively charged colloids and therefore a cationic flocculant is needed to produce flocculation.
- 2) The relation between the zeta potential and a cationic polyelectrolyte flocculant (such as Purifloc C 31) is linear. Owing to this fact, confirmed by some literature data [4,16], measurements could be limited to one or two well chosen experimental points, which, together with the initial zeta potential, allow interpolation of correct flocculation values at zeta potential = 0 mV.
- 3) When analysing the flocculation value or concentration of cationic flocculant at zeta potential = 0 mV, it can be noted that for standard solutions doses varied from 20 to 60 ppm; for radioactive effluent: from 50 to 390 ppm Purifloc C 31. The highly variable values seem to depend on initial zeta potentials, concentration of sludge particles, pH applied and probably the particle diameters as well as the ionic doses supplied in the previous (scavenging-precipitation) stage as discussed above (Chapter 6.2.).
- 4) The linear relation between zeta potential and cationic flocculant concentration presents a "breaking point" at a variable positive potential (between 3.8 mV and 24 mV), where the zeta potential value becomes constant at increasing flocculant dosages. This must be due to saturation of initial negative charges by the cationic flocculant with an overcharge of the latter. The potential limit as well as the corresponding saturation concentration of flocculant depend on the nature of the solution, the initial number, nature and charges of the colloids and probably the particle diameters.
- 5) By addition of an anionic polyelectrolyte, such as Praestol 2900, zeta potentials become still more negative as had to be expected (see Figures 9 and 12). There should be a minimum value as noted here, when further identical charges are repulsed after saturation and then pass into the diffuse layer.
- 6) The addition of non-ionic flocculants, such as Praestol 2700 or Purifloc N 17, had little or no effect on zeta potential values. If zeta potentials become sometimes slightly lower, this may be due to the presence of some active sites.

- 7) According to points 5 and 6 here above, non-ionic as well as anionic flocculants should never be applied to colloidal solutions which are negatively charged, even when initial sedimentation conditions seem good as the negative charge will further increase. The final result can only be a still higher particle dispersion due to mutual repulsion.

6.4. Zeta potential and sedimentation

As stated above, sedimentation rates were measured by means of light transmission in the Lange turbidity cell or by visual observation. A typical example of the turbidity decrease as a function of time is given in Figure 10 for various cationic flocculant concentrations added to a initially negatively charged floc. The positive influence of the addition of flocculant is quite clear. The sedimentation time decreases continuously with increasing flocculant doses from 0 to 100 ppm. The corresponding turbidity half-time is reduced from 3.9 to 1.1 minute. The relative zeta potentials vary from -15 to +10.0 mV. That the minimum turbidity half-time is not found to correspond precisely to zeta potential = 0 mV but to a somewhat higher potential (see also Figure 11) can be explained by the bridging action of the heavy-weight polyelectrolyte. Figure 12 gives an example of sedimentation control by turbidity measurements for the addition of an anionic flocculant. Initially, a good sedimentation rate was obtained but, after a certain time, most of the flocs rised to the surface of the liquid. This fact was due to the highly negative zeta potential (-40 mV).

Using the graduated cylinders, flocculation conditions could be much better observed than in the Lange cell. The sedimentation half-time $t_{v\frac{1}{2}}$ is given in Figure 14 as a function of polyelectrolyte dose and in Figure 15 as a function of the zeta potential for solution h 9. It can be observed here that although sedimentation velocities seem slightly better after the addition of the non-ionic flocculants, zeta potentials become still more negative (from -14 to -24 ppm). It is obvious that this corresponds to highly unstable flocculation conditions even when only a few ppm non-ionic coagulant are used. The addition of cationic flocculant such as Purifloc C 31 has given good results between 200 and 400 ppm for the effluent h 9 examined here. In the present case this concentration is particularly high, which is probably caused by the high pH value. Figure 7b shows how, when decreasing pH at a flocculation dose of 600 ppm C 31, the zeta potential value increases which implies that corresponding flocculation doses would most probably be lower. Parallel experiments with solutions h 10 and h 11 at pH 10 yield much lower flocculation values (80-90 ppm) (see Figure 13).

Figures 16 and 17 show some results on the use of 2 successive flocculants on effluents f 6 and f 7. It can be deduced that a second non-ionic flocculant cannot improve the behaviour of a formerly added non-ionic or anionic flocculant. Zeta potentials remain negative, thus creating unstable flocculation conditions. Only the cationic flocculant gives correct flocculation conditions.

7. CONCLUSIONS

The present work on the control of the zeta potential of sludge particles in suspension in radioactive effluents yielded the information necessary for the improvement of the working conditions of the coprecipitation-flocculation unit in the Ispra-plant for treatment of radioactive effluents.

The measurements, which were satisfactorily performed by the use of a standard type Zeta Meter, enabled the choice of the appropriate type and precise dosage of flocculant to be applied in each particular case. This was not always possible with the formerly applied "beaker tests".

The flow rate of the described plant, formerly 1-1.5 m³/h, has been increased to 2.5-3 m³/h by the use of a cationic polyelectrolyte flocculant such as Purifloc C 31 of Dow Chemicals. Flocculation dosages varied generally from 40 to 100 ppm, but attained in particular cases 400 ppm.

The study is actually continued investigating the precise influence on the zeta potential of the pH and of the nature and concentration of the ions present in solution.

For the zeta potential measurements, a semi-automatic sample changer will be used, which should increase precision and rapidity of the control.

Finally a dynamic sedimentation cell has been designed and built which should enable turbidity and sedimentation controls, in parallel with zeta potential measurements, under various working conditions. This apparatus should simulate plant conditions better than the formerly used static sedimentation tests.

ACKNOWLEDGEMENT

Mrs. J. Vaccarezza and C. Monfrini are acknowledged for the preparation of the effluents and for controlling the results under operational conditions.

BIBLIOGRAPHY

- [1] Krawczynski S., Amavis R., Vaccarezza J. and Vanuzzi S.,
EUR 1228 d (1965).
- [2] Lopes Cardozo R., Vaccarezza J. and Vanuzzi S.,
EUR 3175 e (1966).
- [3] Blanco R.E., Davies W. Jr., Godbee H.W. et al.,
Symposium on Practices in the Treatment of Low and Intermediate Level Radioactive Wastes,
I.A.E.A., SM 71/26, Vienna (1965).
- [4] Riddick T.M.,
J. AWWA, 53 (8) 1007 (1961).
- [5] Riddick T.M.,
Chemical Engineering, 121 (1961).
- [6] Riddick T.M.,
Chemical Engineering, 141 (1961).
- [7] Riddick T.M.,
T.A.P.P.I. (Technical Association of the Pulp and Paper Industry), 47 (1) 171 A (1964).
- [8] Jacobson N.A. and Schmut R.,
T.A.P.P.I., 47 (1) 210 A (1964).
- [9] Kane J.C., La Mer V.K. and Linford H.B.,
Journal of American Chemical Society, 86, 3450 (1964).
- [10] Black A.P. and Chen Ching-Lin,
Journal AWWA, 57 (3) 354 (1965).
- [11] Baker R.A., Campbell S.J. and Anspach F.R.,
Journal AWWA, 57 (3) 363 (1965).
- [12] Glasstone S.,
Introduction to Electro-Chemistry,
Ed. D. Van Nostrand Co. Princeton, N.J. (1942).
- [13] Mark H.F. and Verwey E.J.W.,
Advances in Colloid Science,
Ed. Interscience Publishers Inc. New York (1950).
- [14] Verwey E.J. and Overbeek T.G.,
Theory of the Stability of lyophobic Colloids,
Ed. Van Nostrand Co. Princeton, N.J. (1948).
- [15] Mysel K.,
Introduction to Colloid Chemistry,
Ed. D. Van Nostrand Co. Princeton N.J. (1959).
- [16] Kruyt H.R.,
Colloid Science Vol. I, Chap. VIII, Elsevier Press.,
New York (1952).
- [17] Riddick T.M. et al.,
The Zeta Meter Manual 2nd Ed. (1968),
Zeta Meter Inc., 1720 First Avenue, New York N.Y. 10028.
- [18] Riddick T.M.,
Control of Colloid Stability through Zeta Potential, Vol. I,
Ed. Livingston Publishing Cy. Wynnewood, Pennsylvania, U.S.A.
(1968).

Figure 1

FLOW SHEET OF DECONTAMINATION PLANT

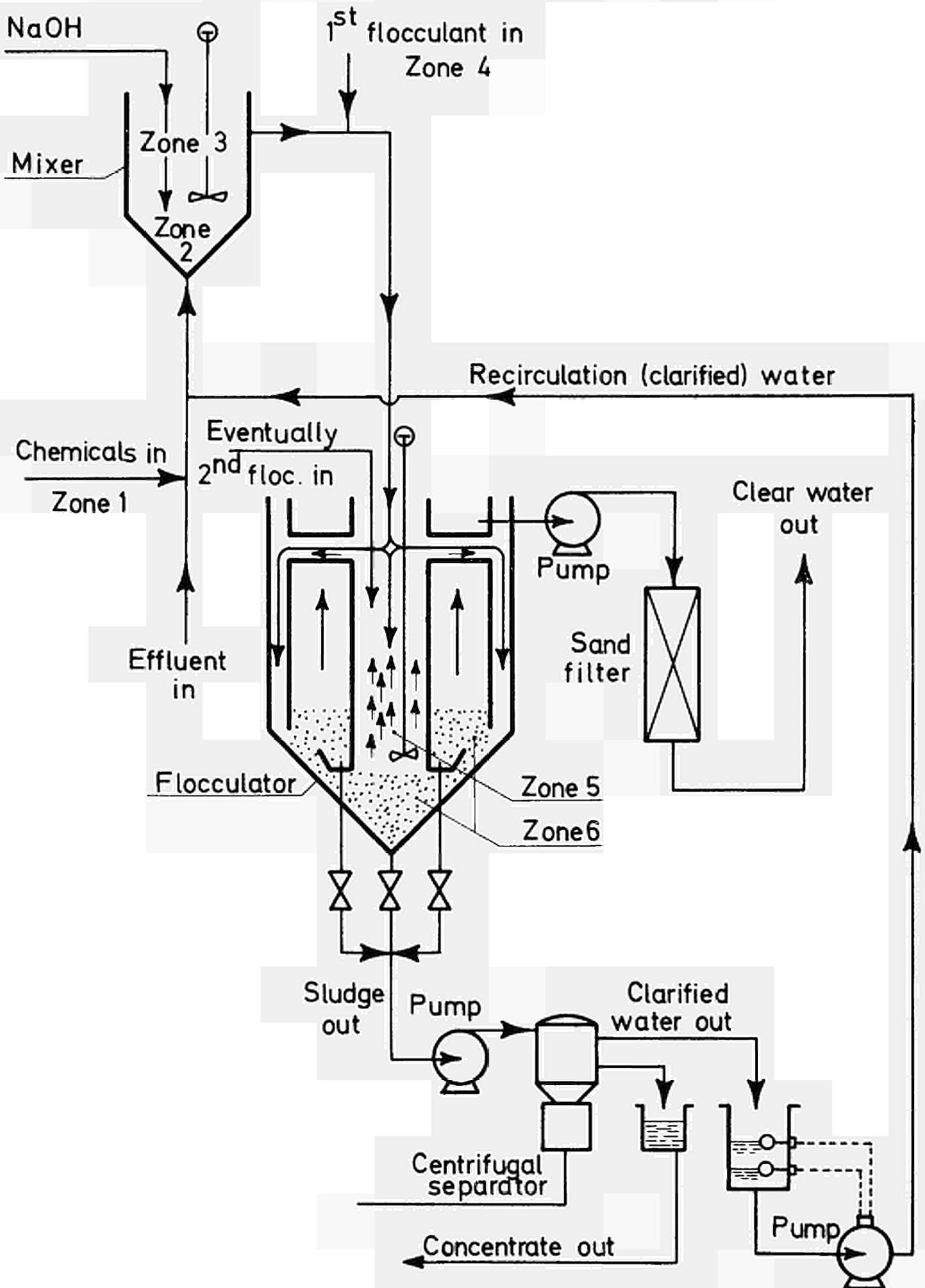


Figure 2
CONCEPT OF THE ZETA POTENTIAL

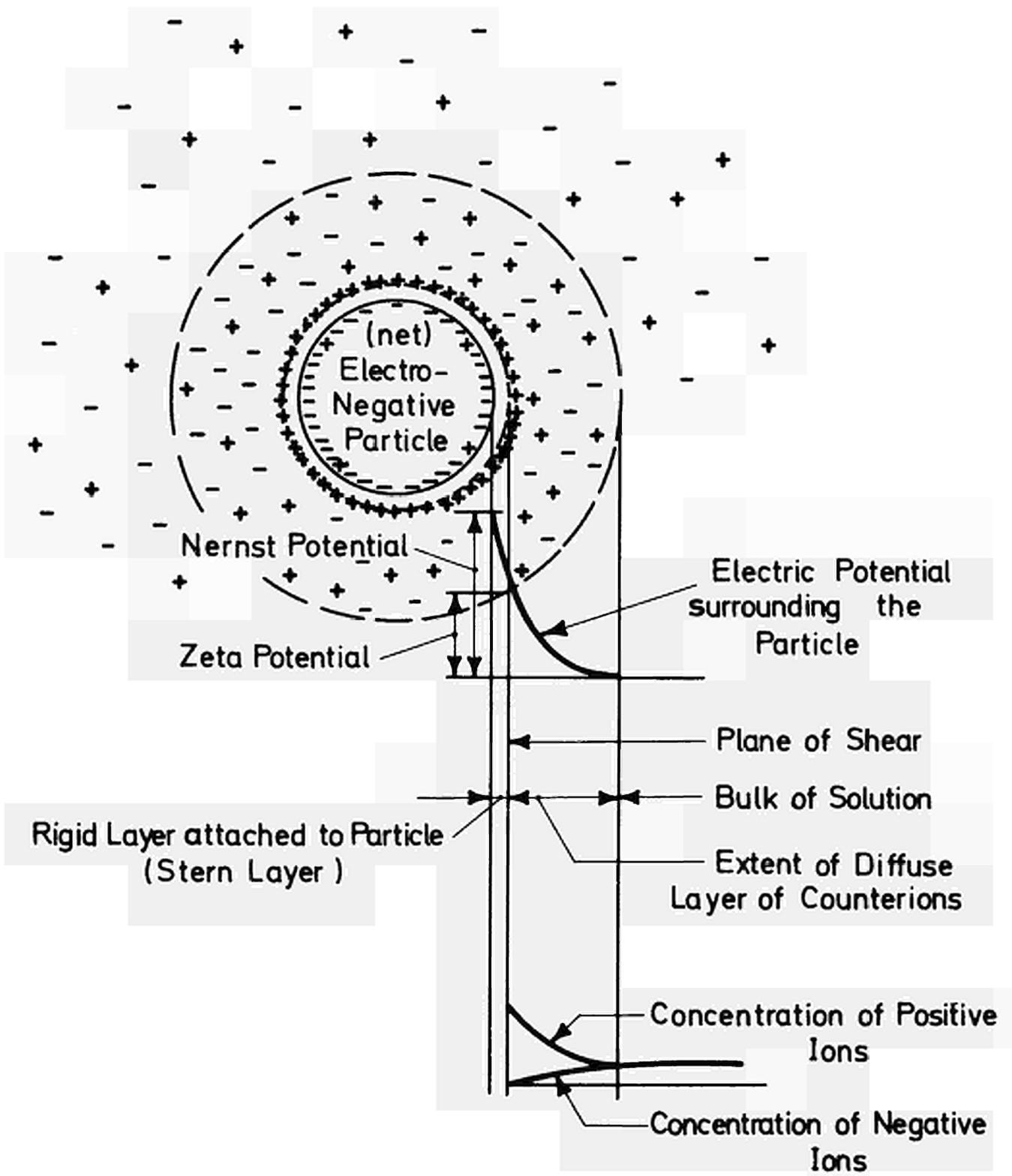
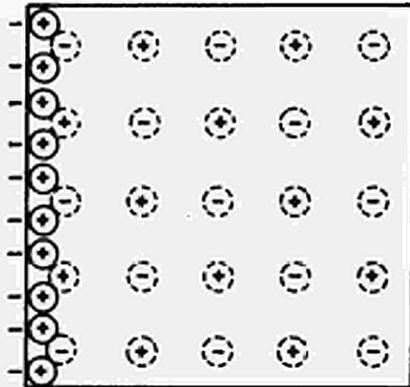


Figure 3

SCHEMATIC DOUBLE-LAYER STRUCTURES

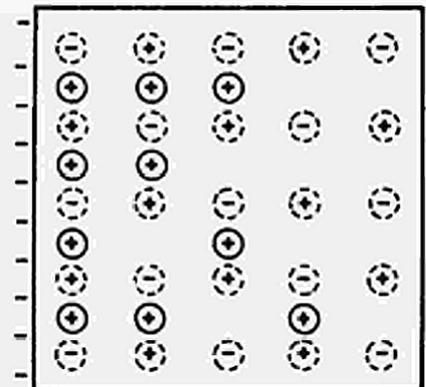


a)

Formation of a compact double-layer when wall becomes charged in the absence of thermal agitation.

b)

Formation of a diffuse double-layer by counterions alone.



c)

A Helmholtz simplified double-layer.

⊕ added counterions
⊖ unchanged ions

Figure 4
RIDDICK TYPE ELECTROPHORESIS CELL

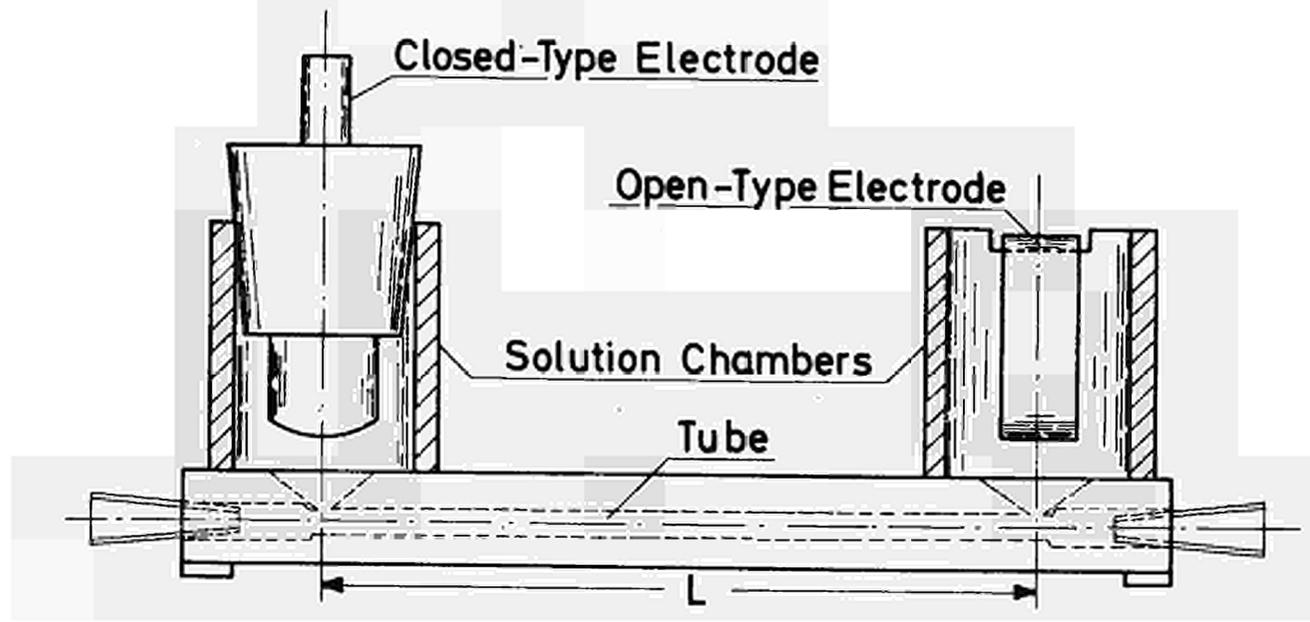


Figure 5

**DISTRIBUTION CURVES FOR STANDARD SOLUTION a13
WITHOUT AND WITH CATIONIC FLOCCULANT C 31**

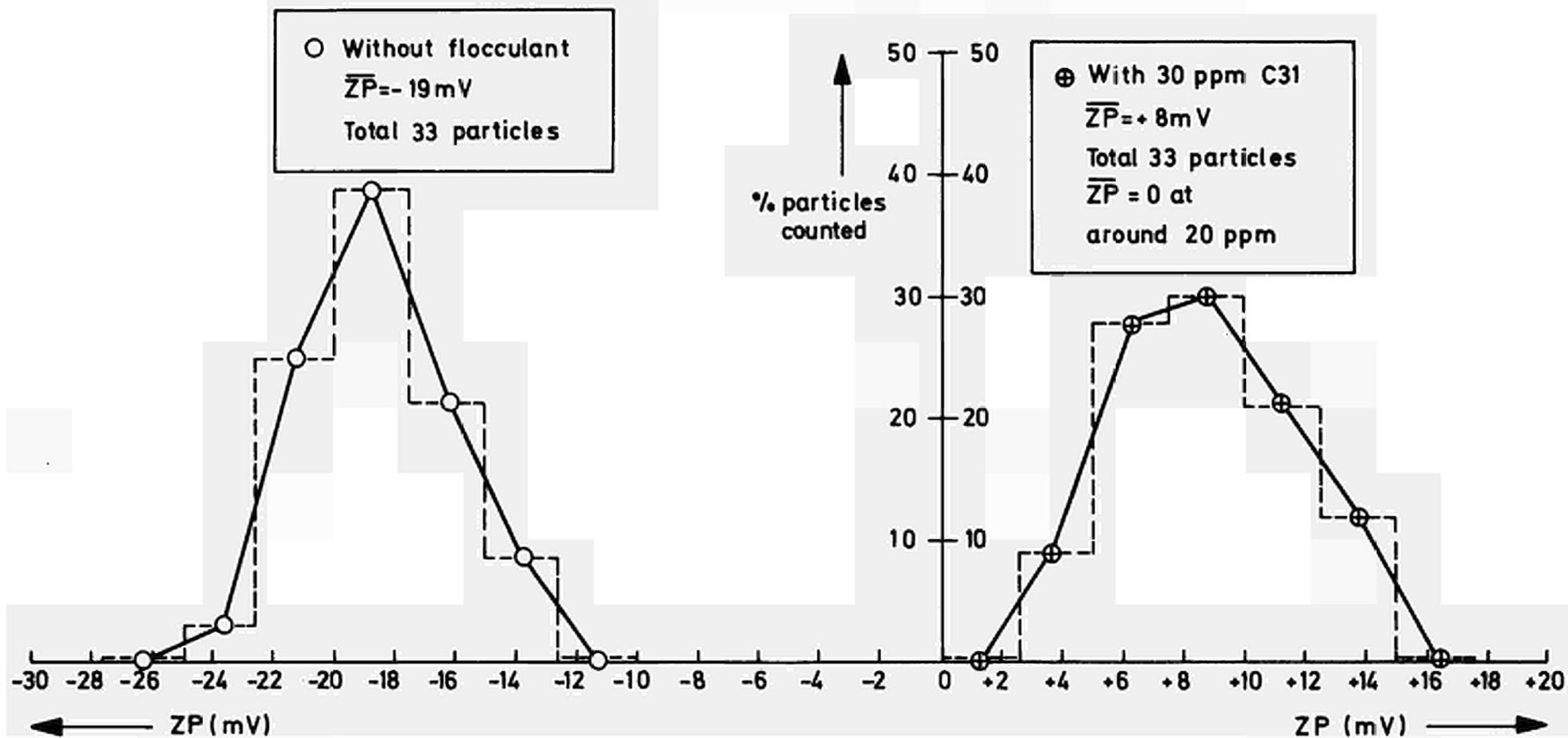
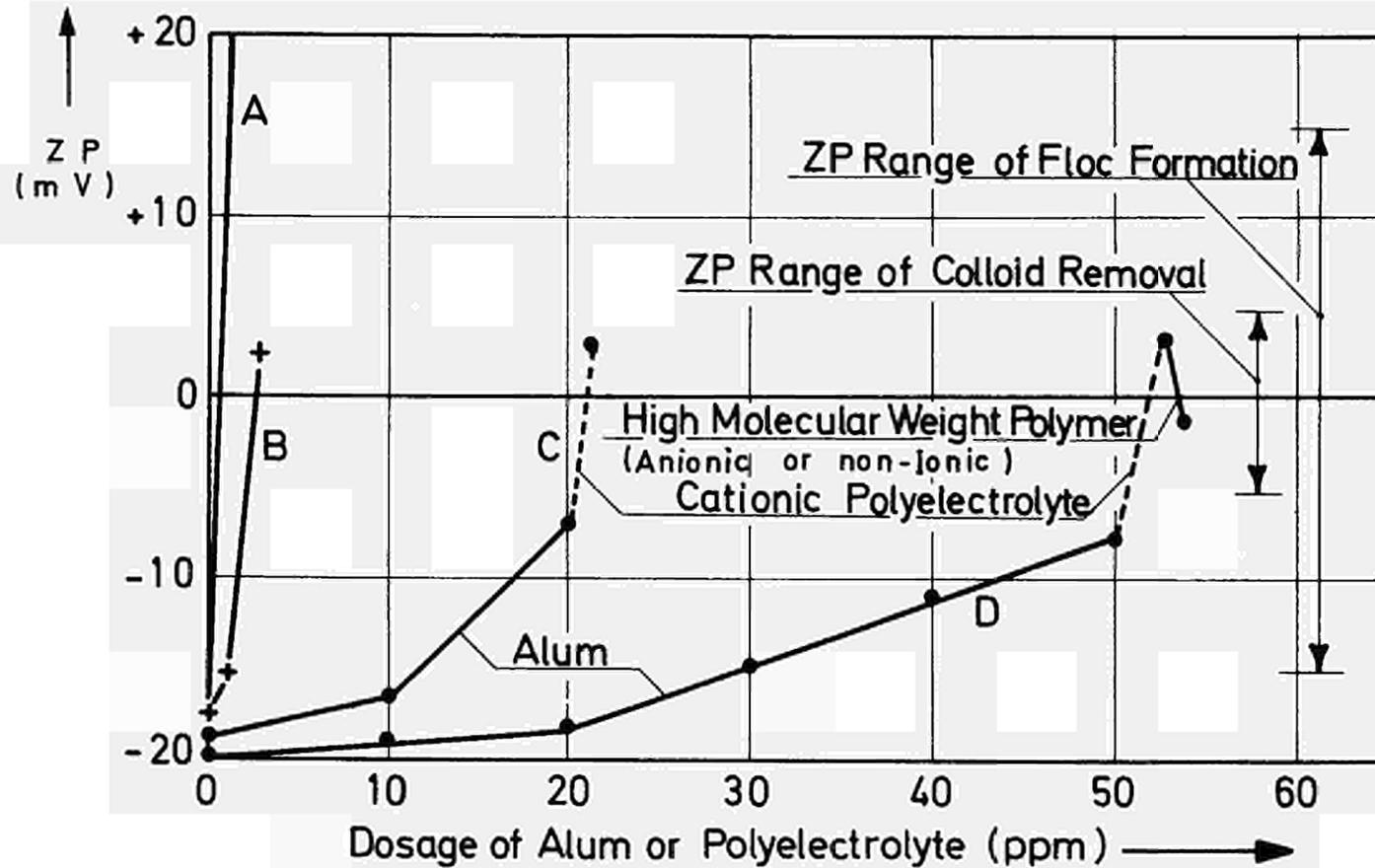


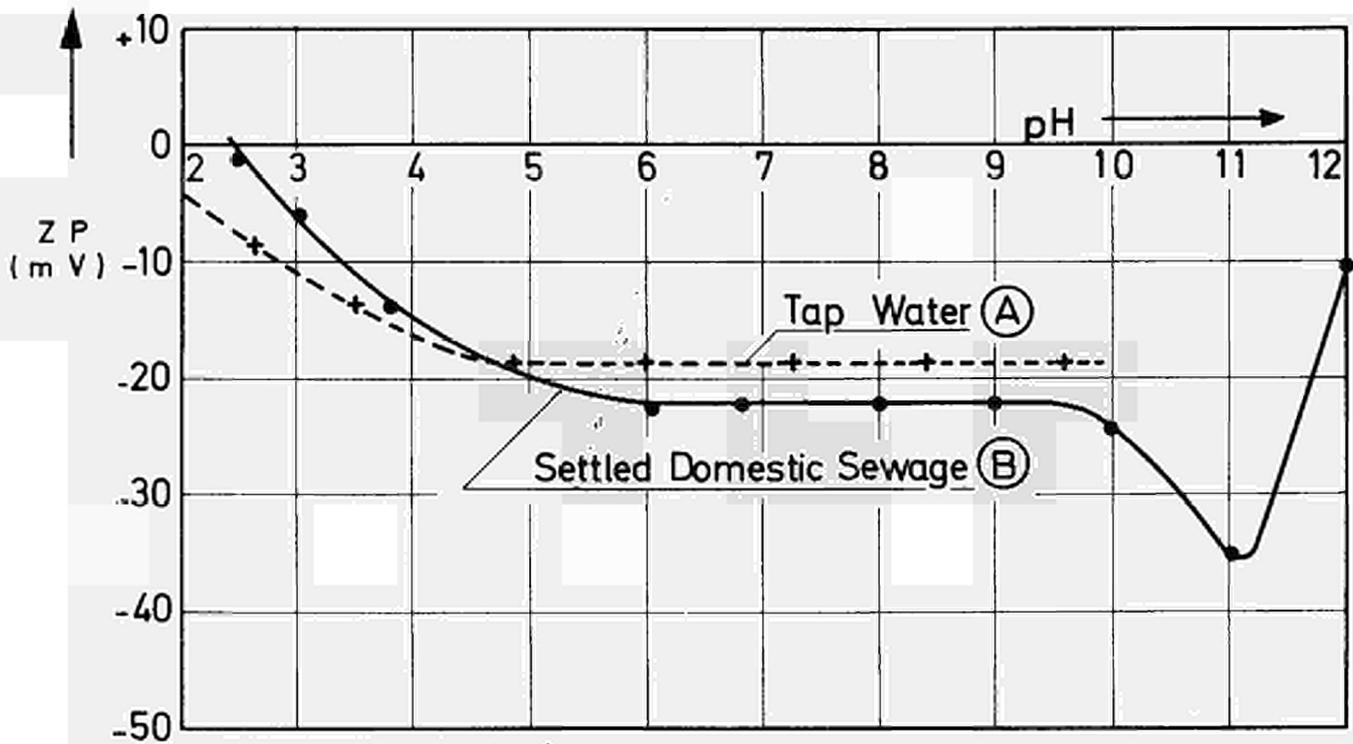
Figure 6

EFFECTS OF VARIOUS FLOCCULANTS ON ZETA POTENTIAL [4]

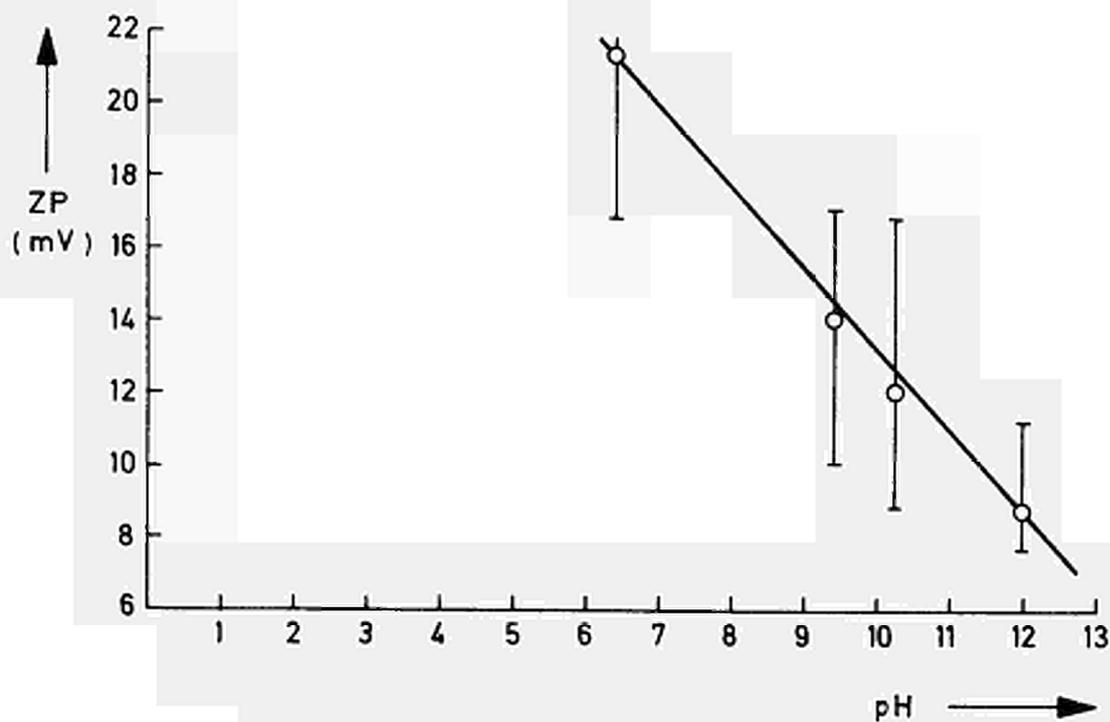


- A : distilled water + a Cationic Polyelectrolyte (Polyamine)
- B : tap water + a Cationic Polyelectrolyte (Polyamine)
- C : tap water + Alum (2 dosages) + event. Cationic Polyelectrolyte
- D : tap water + Alum and Polyelectrolytes

Figure 7
pH EFFECT ON ZETA POTENTIAL



a) ZP - pH Curves for Water and Sewage [7]



b) R.A. Effluent h 9 + 600 ppm C 31
 Effect of pH variation on zeta potentials by addition
 of HNO_3 at initial pH= 12

Figure 8

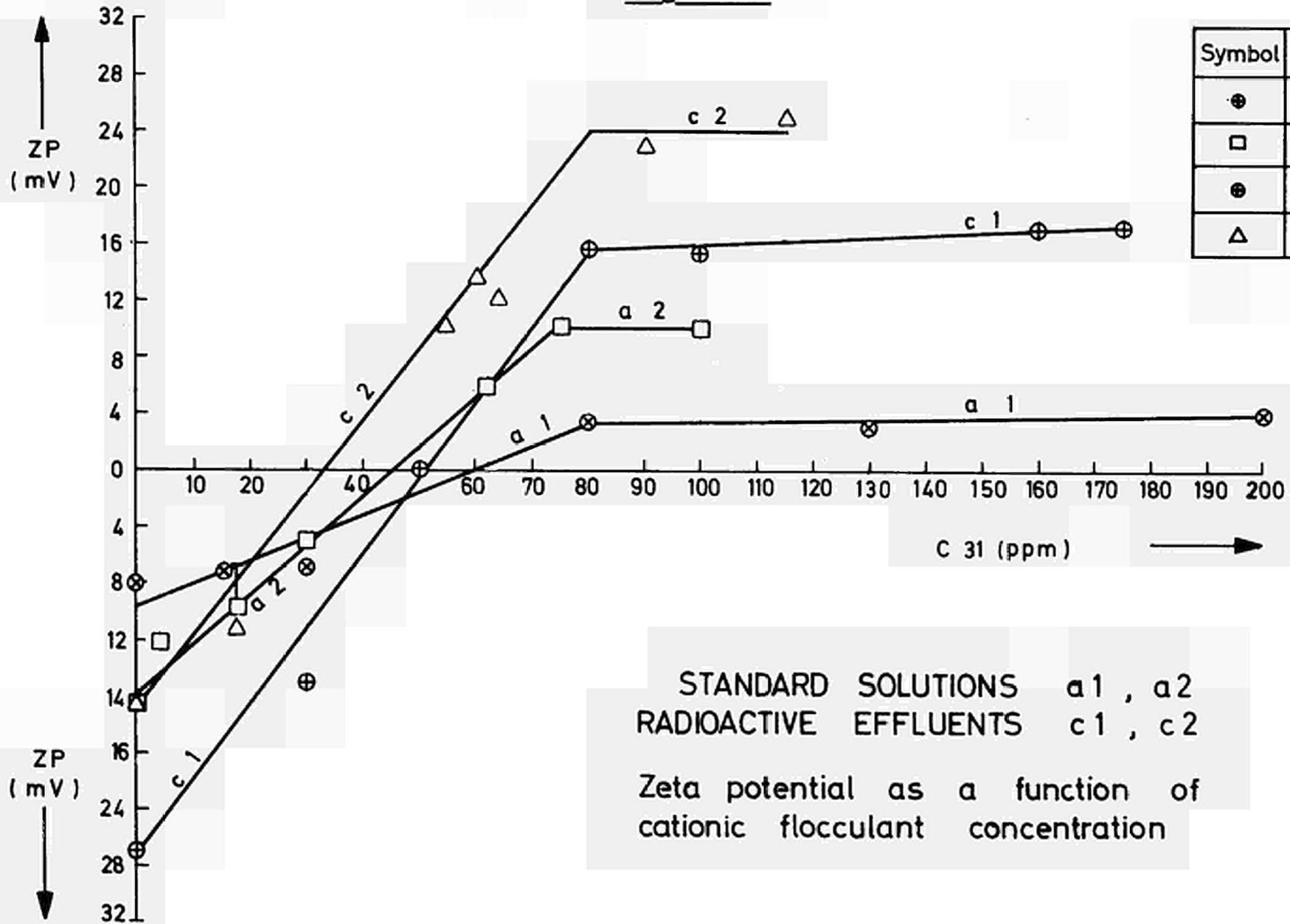


Figure 9

RADIOACTIVE EFFLUENT e5

Effects of cationic (C), anionic (A) and non-ionic (N) flocculant concentration on zeta potential

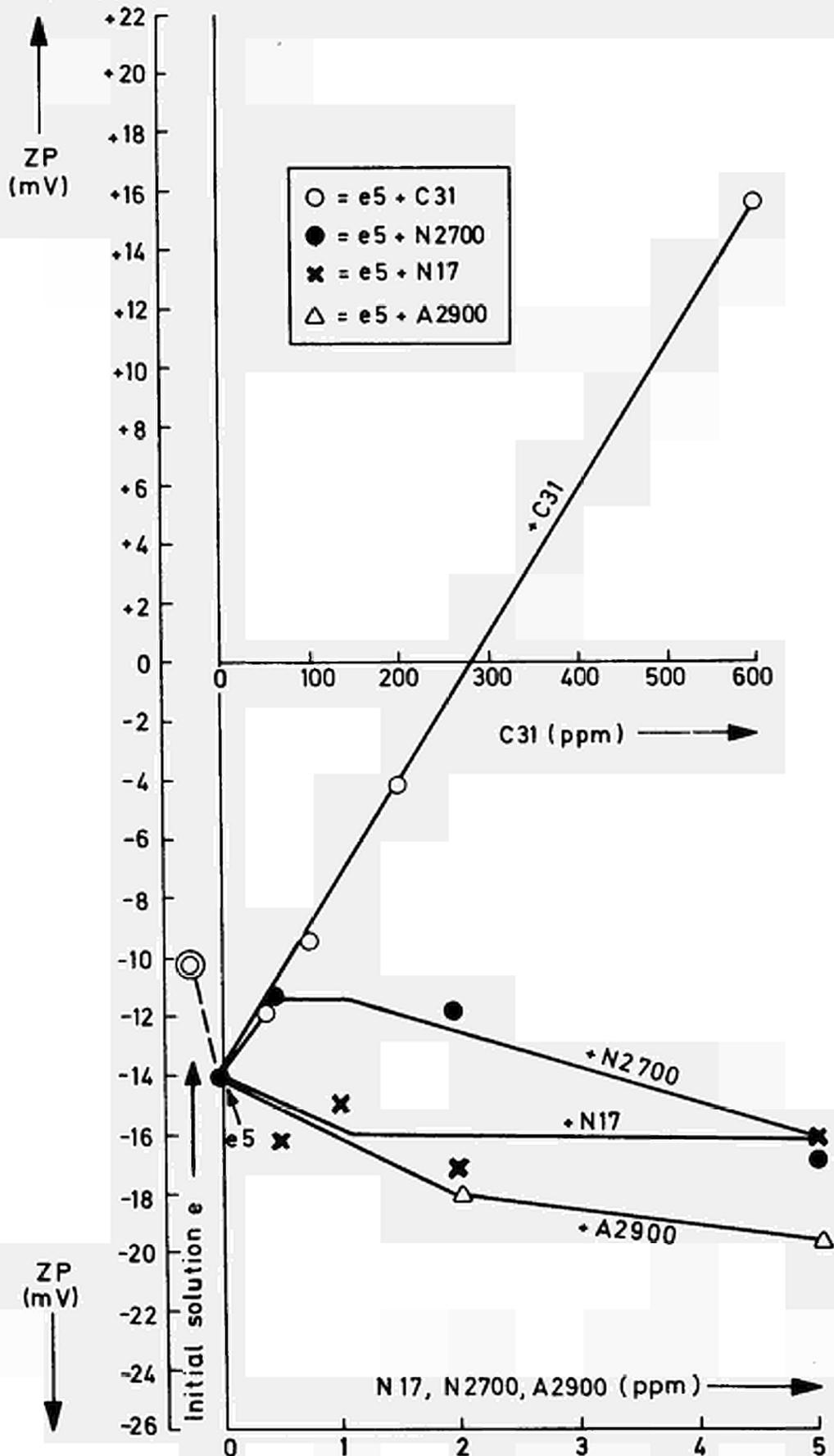


Figure 10

STANDARD SOLUTION a2

Turbidity as a function of time for various concentrations of cationic flocculant C 31

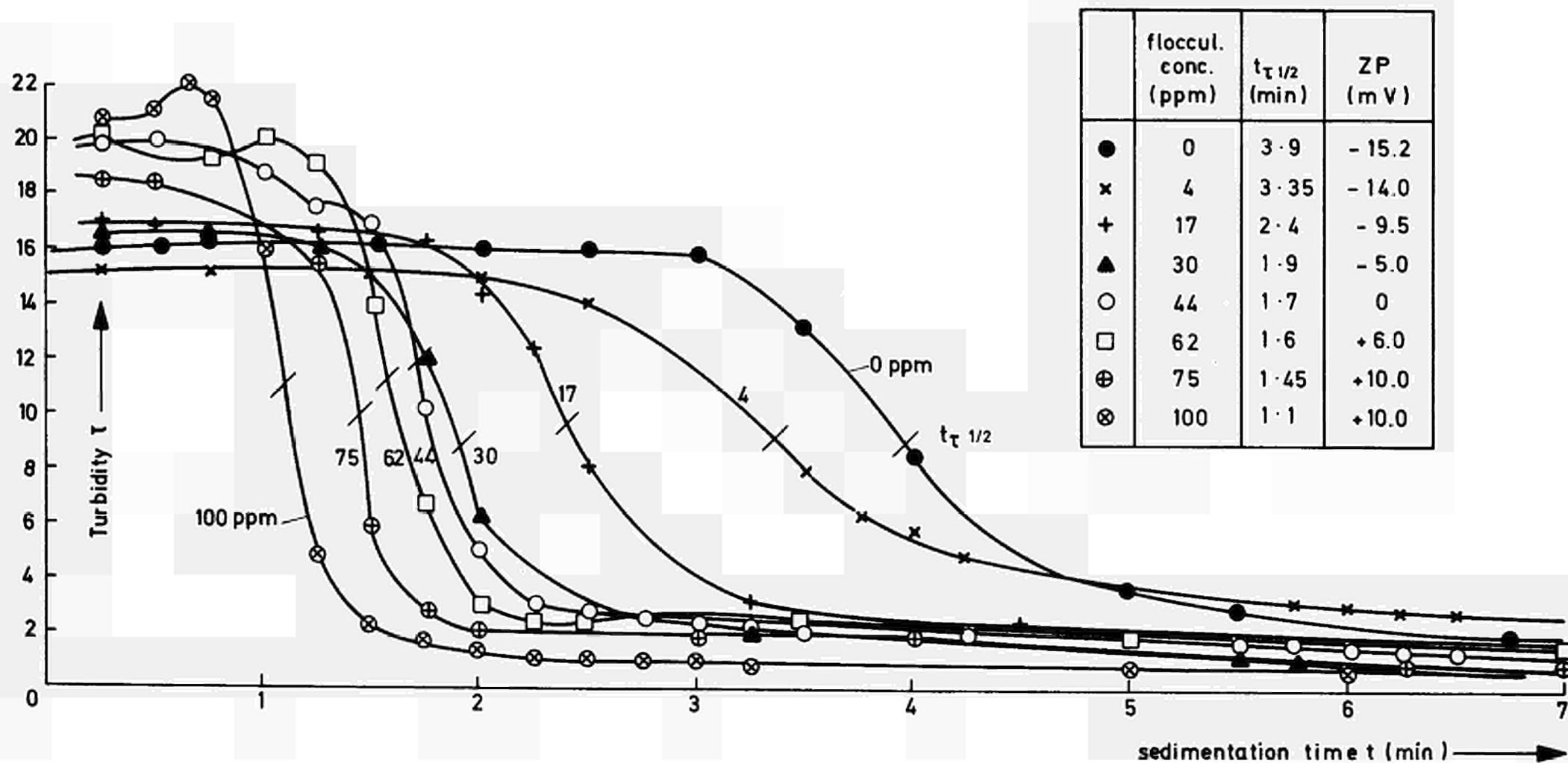


Figure 11

SOLUTIONS a2, c1, c2

Zeta potentials as a function of turbidity half-times for corresponding concentrations of cationic flocculant C 31

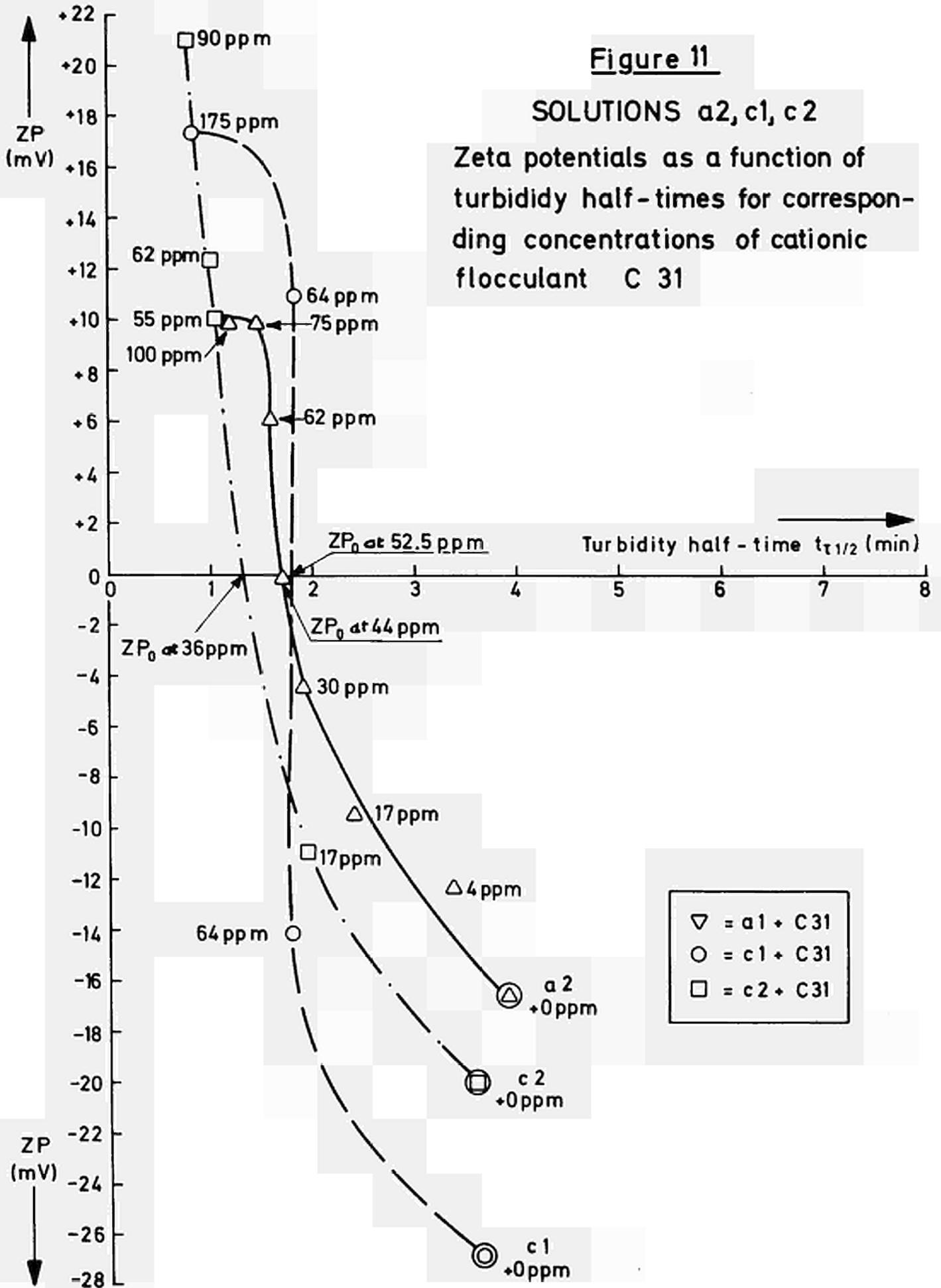


Figure 12 - RADIOACTIVE SOLUTION d3

Sample direct from treatment station containing already 0.5 ppm A2900

Turbidity τ as a function of sedimentation time t for various additional concentrations of anionic flocculant A 2900

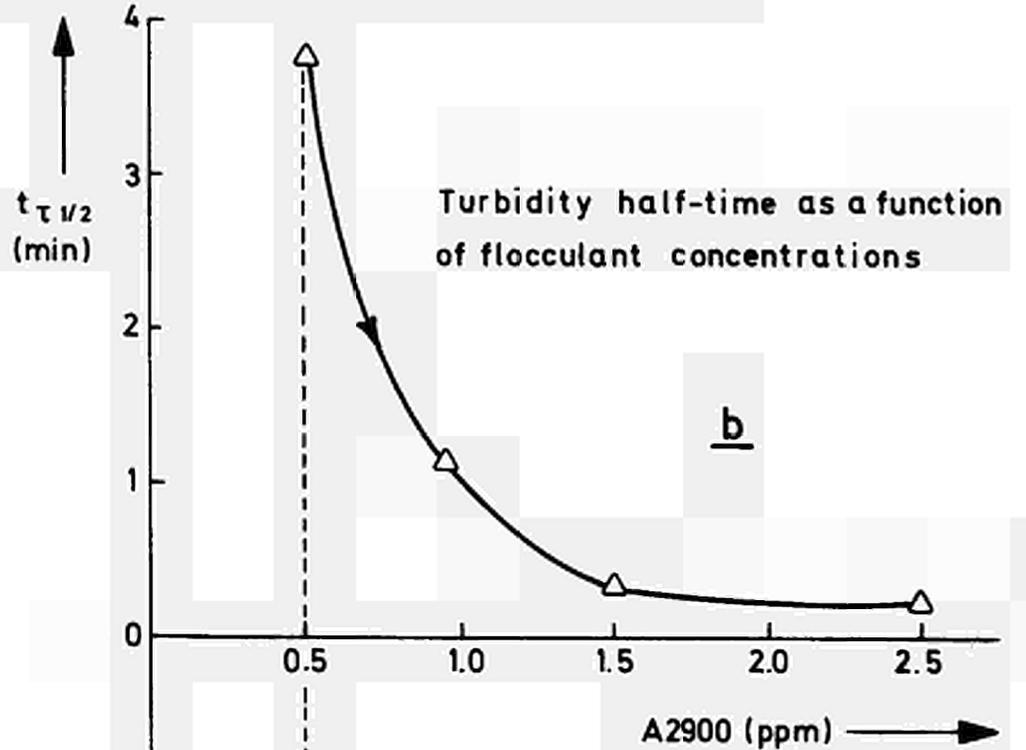
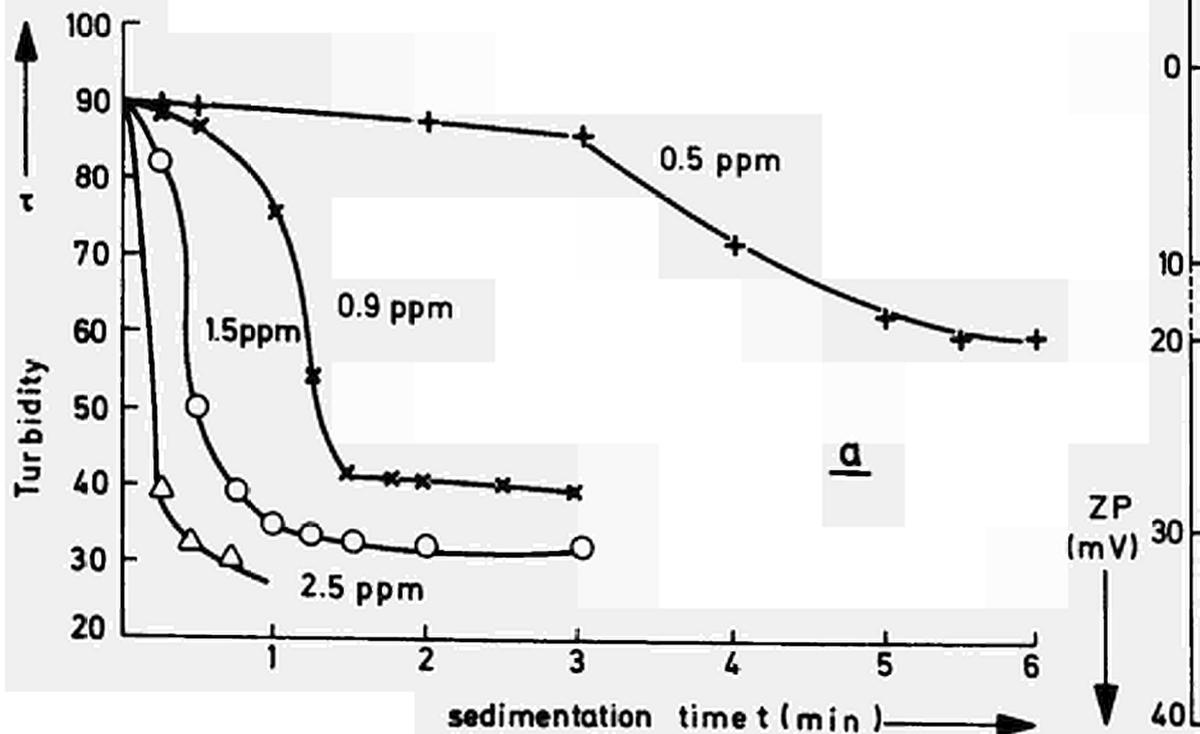


Figure 13

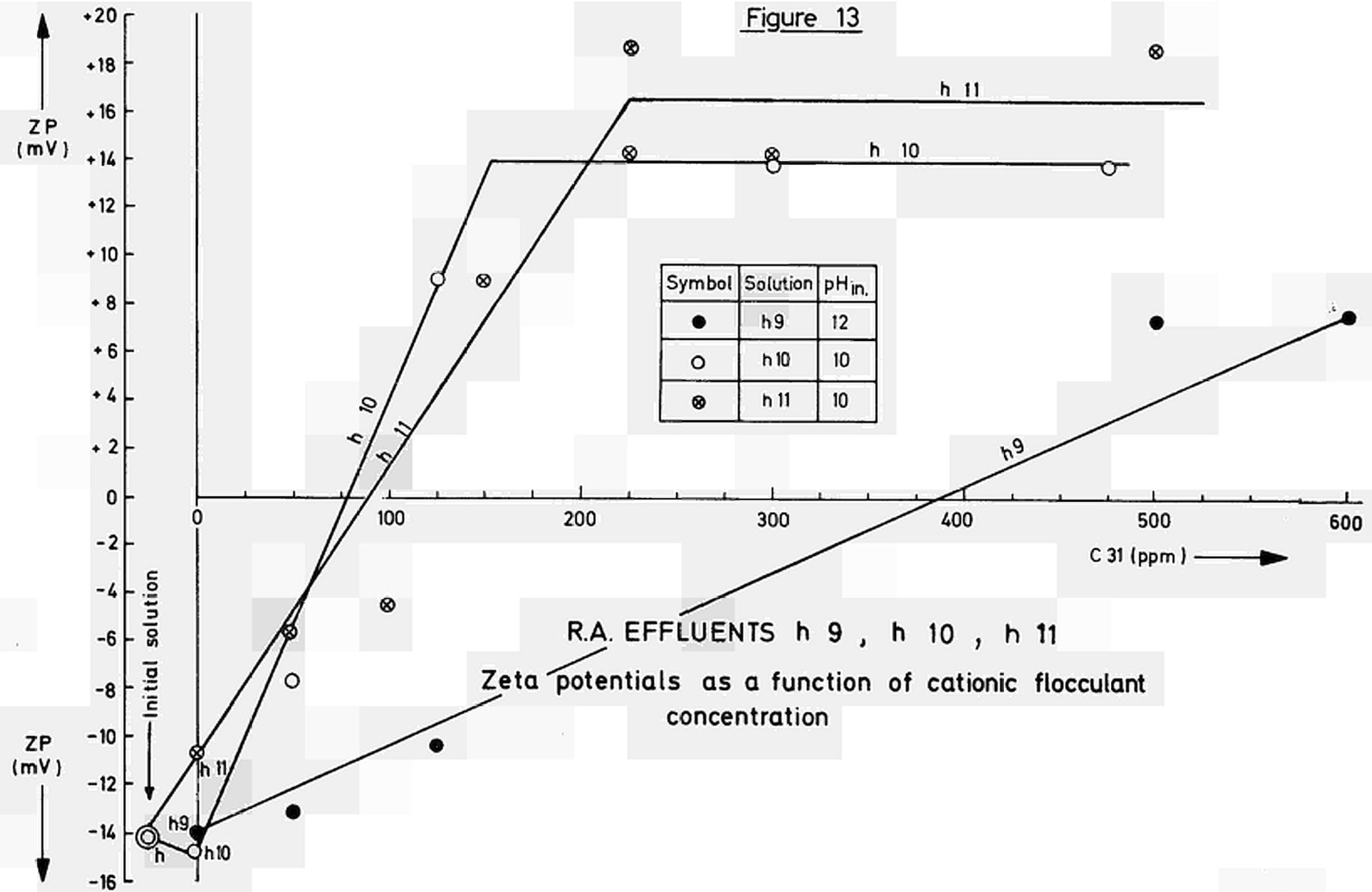


Figure 14

RADIOACTIVE SOLUTION h 9
Sedimentation half-times as a function
of flocculant concentrations

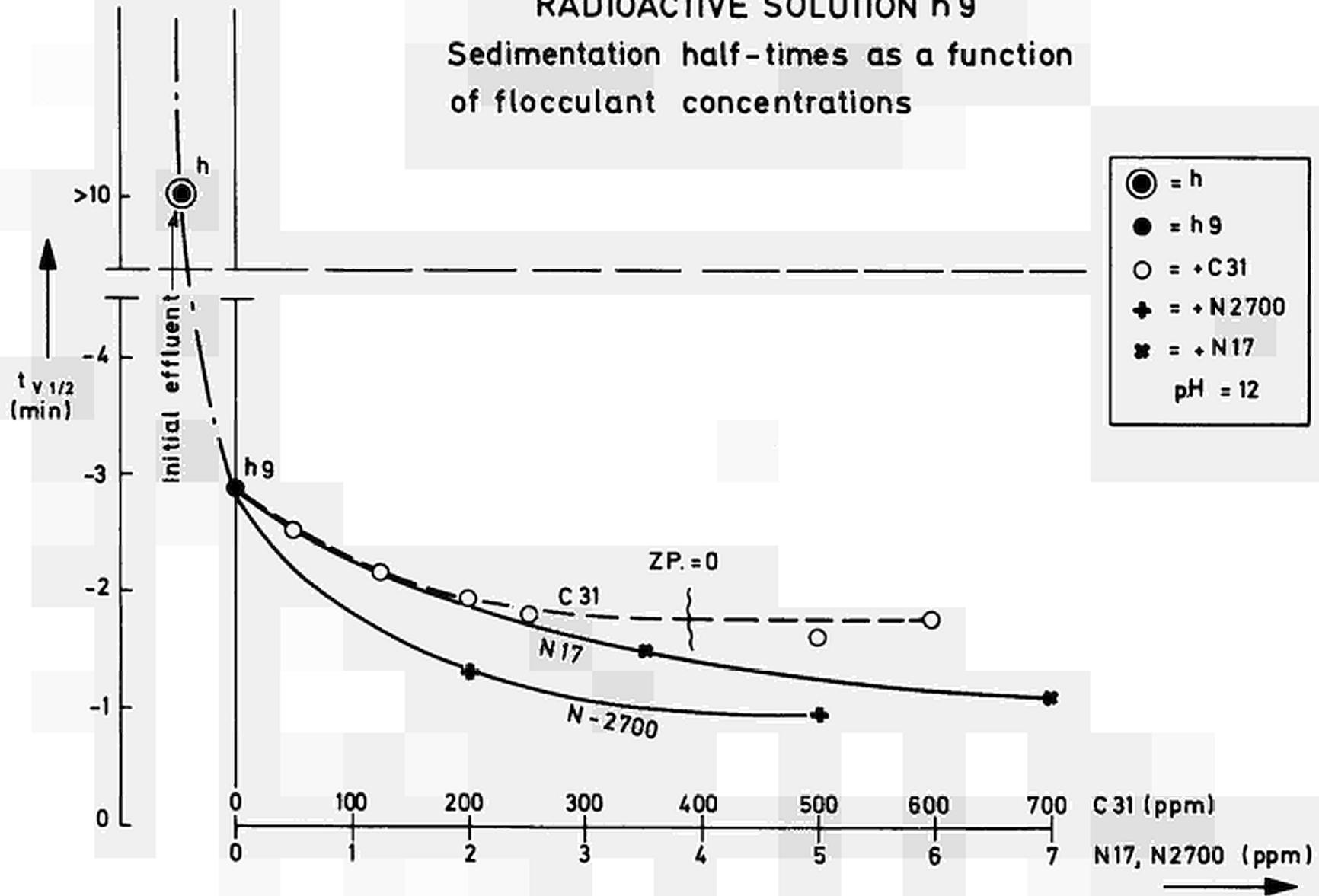


Figure 15

RADIOACTIVE SOLUTION h9

Sedimentation half-times ($t_{v1/2}$) as a function of zeta potentials for cationic (C) and non-ionic (N) flocculants at corresponding concentrations (pH=12)

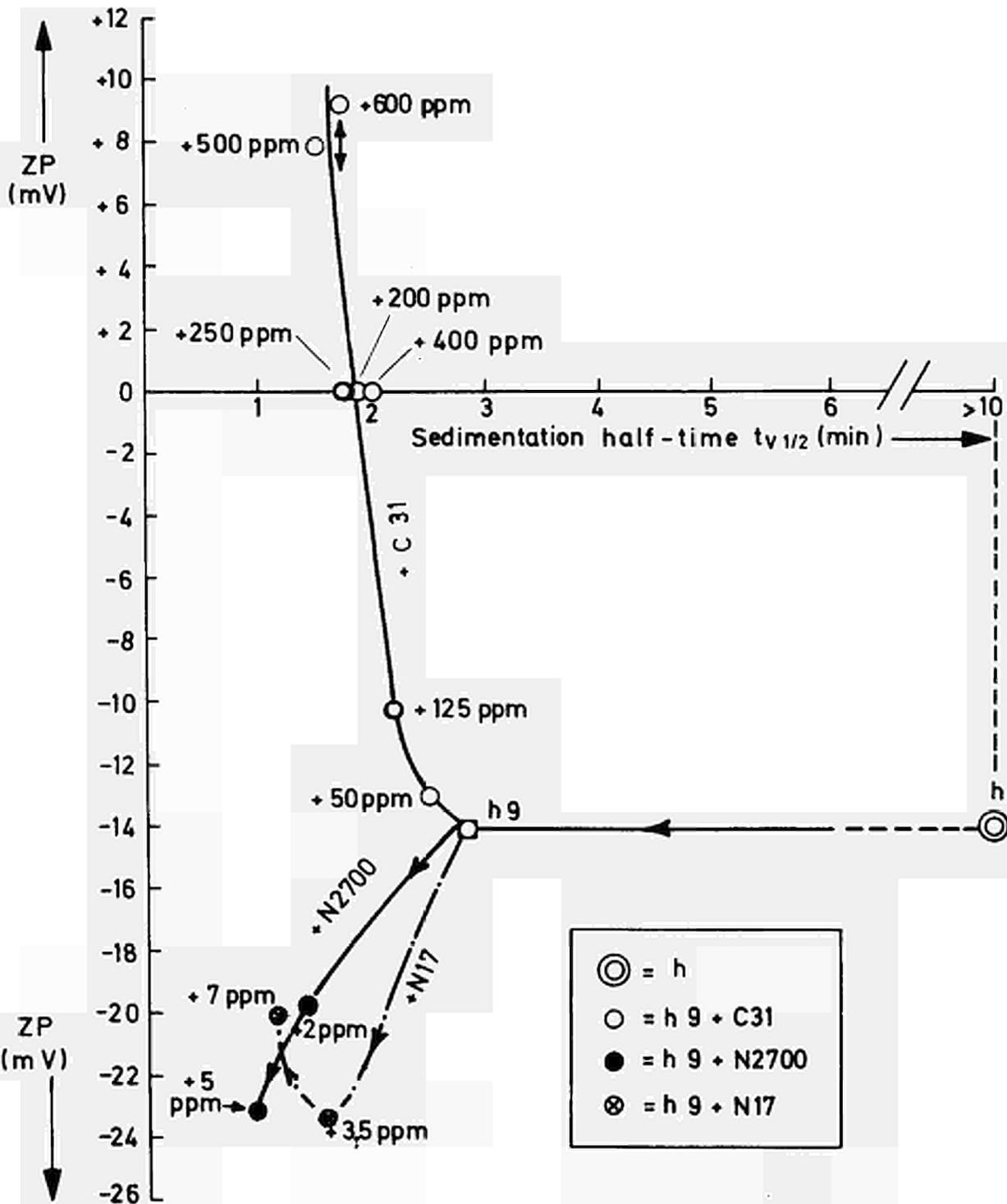
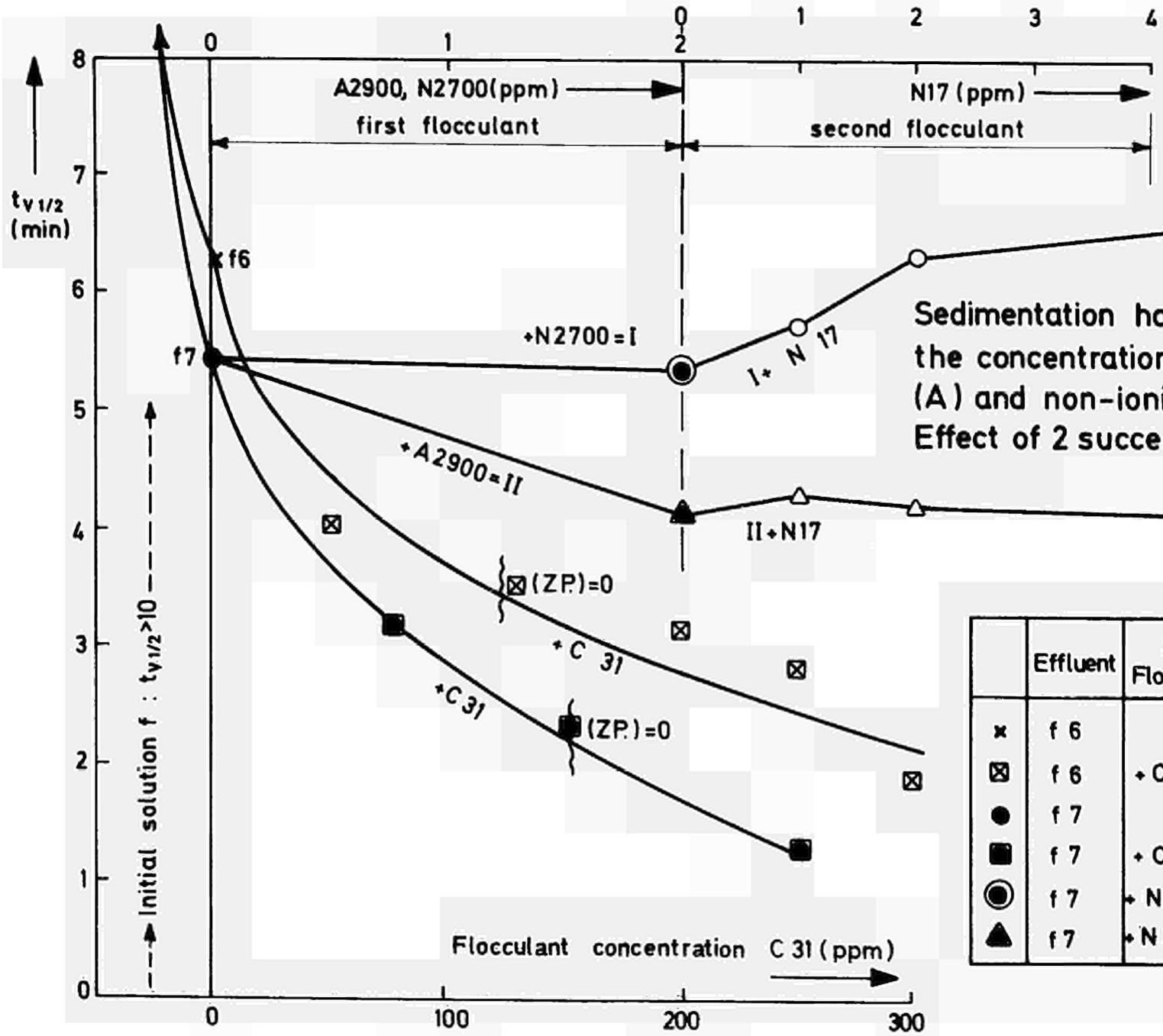


Figure 16

**RADIOACTIVE SOLUTIONS
f6 AND f7**



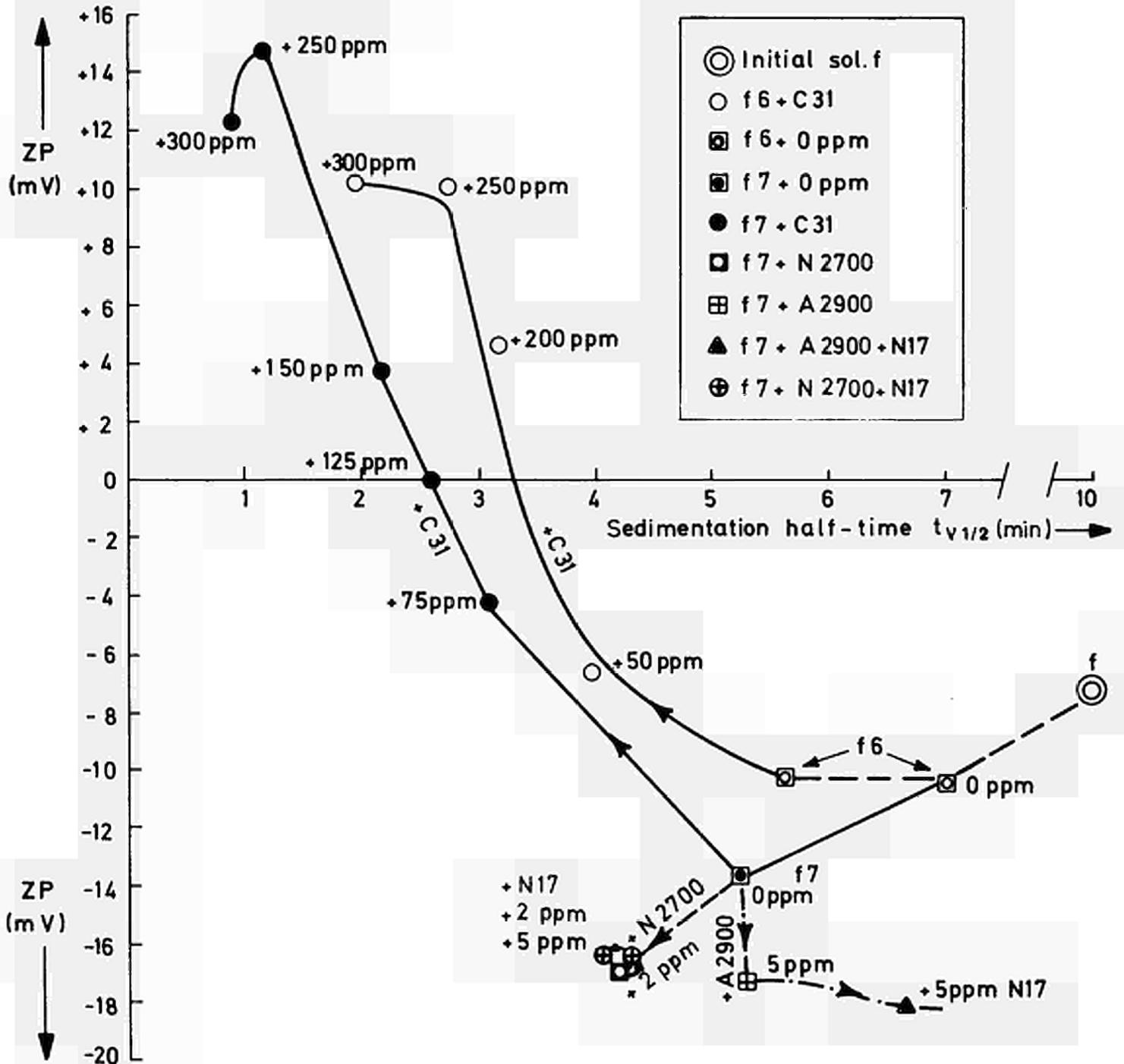
Sedimentation half-times as a function of the concentration of cationic (C) anionic (A) and non-ionic (N) flocculants
Effect of 2 successive flocculants

	Effluent	1st Floccul.	2nd Floccul.	
x	f 6	0	0	
⊠	f 6	+ C 31	0	
●	f 7	0	0	
■	f 7	+ C 31	0	
⊙	f 7	+ N 2700 = I	+ N 17	○
▲	f 7	+ N 2900 = II	+ N 17	△

Figure 17

RADIOACTIVE SOLUTIONS f6 AND f7

Sedimentation half-times as a function of zeta potentials for various flocculants at increasing concentrations



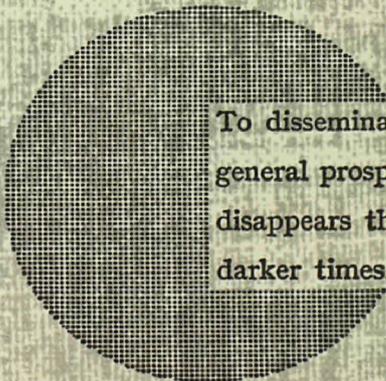
NOTICE TO THE READER

All Euratom reports are announced, as and when they are issued, in the monthly periodical **EURATOM INFORMATION**, edited by the Centre for Information and Documentation (CID). For subscription (1 year : US\$ 15, £ 6.5) or free specimen copies please write to :

Handelsblatt GmbH
"Euratom Information"
Postfach 1102
D-4 Düsseldorf (Germany)

or

Centrale de vente des publications
des Communautés européennes
37, rue Glesener
Luxembourg



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

SALES OFFICES

All Euratom reports are on sale at the offices listed below, at the prices given on the back of the front cover (when ordering, specify clearly the EUR number and the title of the report, which are shown on the front cover).

CENTRALE DE VENTE DES PUBLICATIONS DES COMMUNAUTES EUROPEENNES

37, rue Glesener, Luxembourg (Compte chèque postal N° 191-90)

BELGIQUE — BELGIE

MONITEUR BELGE
40-42, rue de Louvain - Bruxelles
BELGISCH STAATSBLAD
Leuvenseweg 40-42 - Brussel

LUXEMBOURG

CENTRALE DE VENTE
DES PUBLICATIONS DES
COMMUNAUTES EUROPEENNES
37, rue Glesener - Luxembourg

DEUTSCHLAND

BUNDESANZEIGER
Postfach - Köln 1

NEDERLAND

STAATSDRUKKERIJ
Christoffel Plantijnstraat - Den Haag

FRANCE

SERVICE DE VENTE EN FRANCE
DES PUBLICATIONS DES
COMMUNAUTES EUROPEENNES
26, rue Desaix - Paris 15°

UNITED KINGDOM

H. M. STATIONERY OFFICE
P.O. Box 569 - London S.E.1

ITALIA

LIBRERIA DELLO STATO
Piazza G. Verdi, 10 - Roma

EURATOM — C.I.D.
29, rue Aldringer
Luxembourg

CDNA04401ENC