T.P. 1364

Flocculation Studies on Iron Ore Fines Using Synthetic Polymeric Flocculants

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ABSTRACT

Flocculation studies on Donimalai haematitic iron ore fines were carried out using various types of synthetic polymeric flocculants. Califloc was found to be an efficient flocculant and more systematic, statistically designed experiments were carried out in order to evaluate the role of various parameters such as pH, flocculant and calcium concentrations on settling rate and supernatent clarity. Physico-chemical parameters affecting the flocculation process are discussed.

INTRODUCTION

Our country is on the threshold of large scale, mechanized mining and minerals processing activity with respect to iron ores, to meet both the internal demands and export commitments. Significant amounts of iron ore fines are generated while mining as well as processing of iron ores. These fines, high in iron content, are a good source of iron itself and need special processing before reduction. Also, accumulations of fines lead to environmental problems due both to dust generation and water pollution.

This work was undertaken to study the amenability of typical haematitic ore fines of India to flocculation by indigenously available flocculants. No previous work in this direction has been reported. Several types of indigenously available synthetic polymeric flocculants were screened for this purpose.

EXPERIMENTAL

Iron ore samples of the following composition were received from M/s National Mineral Development Corporation, Donimalai :

Fe	61.3%
SiO_2	4.2%
Al_2O_3	4.6%
CaO	0.5%

—400 mesh sieved fractions were used in the flocculation tests.

Details of the various synthetic flocculants used in this study are given in Table I. Polymer samples were weighed accurately and added to known volumes of water and stirred to prepare clear solutions. Analar grade calcium chloride was used in some tests. Hydrochloric acid and sodium hydroxide were used as pH modifiers. Distilled and deconised water were used in the preparation of all solutions.

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Preliminary tests were performed to

(a) assess the relative flocculation efficiency of the various polymers.

(b) to understand the role of various parameters such as pH, calcium and flocculant concentrations and to investigate the effect of the sequence of addition with respect to calcium and flocculant additions.

(c) to select proper experimental conditions and procedures.

The ore sample (50 grams at 5% pulp density) was placed in a 1000 ml. graduated cylinder and water added to near the 1000 ml mark so that subsequent addition of reagents would give a pulp volume of 1000 ml. The cylinder was tumbled ten times to ensure homogenized dispersion of particles. The flocculant dosage was added in one instalment and the cylinder tumbled ten times before allowed to settle. The level of the pulp was noted for every fifteen seconds till the settling was complete. The cylinder was once again tumbled ten times and the pulp level noted as before. Turbidity of the supernatent solutions was measured using a Toshniwal make Turbidity meter.

RESULTS AND DISCUSSION

Settling curves for different flocculants were plotted as shown in Fig. 1. The relative strength of the flocs formed could be related to the area between the first and second settling curves; smaller areas mean higher floc strength since the flocs do not disintegrate even with ten tumblings after first flocculation. This in turn is related to the steepness of the settling curves (settling

TABLE I—Details of synthetic polymers used in this work

S. No.	Name of floccu-lant	Suppliers	Chemical composition	Molecular weight	Nature of charge	Remarks
1.	Caflo N-6	Commercial Corporates, Calcutta	Major ingredient-galactomannan polysaccharide	2 to 3 lakhs	Anionic and cationic	Powder form ; efficient flocculant
2.	Caflo N-7					
3.	U.D.A. (powder)	HICO Products Private Limited, Bombay	Condensate-Naphthalene sulphonate	Approximate Mol. wt. 490—500	—	good dispersant ; inefficient flocculant
4.	U.D.A. (Liquid)					
5.	955-D		Hydrolysed acrylamide	1.5 million to 2 million	—	not efficient flocculant
6.	Hyfloc A		—	—	non-ionic	Yellowish white viscous liquid ; good flocculant
7.	Polyacrylamide(N)	Laboratory prepared sample—know how with G.C.I. chemicals. Nagpur	Polyacrylamide	—	Probably non-ionic	Crystalline type : easily soluble in water ; very efficient flocculant
8.	Polyacrylamide (commercial)	G.C.I. Chemicals, Nagpur	Polyacrylamide	—	Non-ionic	Viscous liquid ; Not tested
9.	Califloc A	Calico Chemical, Bombay	$(CH_2CHCONH_2)_x$ $(CH_2CHCOONa)_y$	5×10^7	Anionic	Rubbery cake type ; have 50% solid content in water ; very efficient flocculant
10.	Morfloc—A	The Dharamsi Morarji Chemical Co. Ltd., Bombay	Polymer and Copolymer of acrylic acid and acrylamide	2.5—3 millions	Non-ionic	Viscous liquid ; in efficient flocculants
11.	Morfloc-PG				Anionic	Viscous liquid ; quite efficient flocculants
12.	Morfloc A-30				Anionic	Viscous liquid ; quite efficient flocculant
13.	Morfloc A-40 H				Anionic	Viscous liquid ; quite efficient flocculant
14.	Morfloc A-100				Anionic	Viscous liquid good flocculant

ate); greater the steepness, larger the relative density and size of the flocs.

The settling rate and turbidity were plotted as a function of increasing dosage of the flocculants as shown in Figs. 2 and 3. It could be readily observed that 955-D and UDA (powder and liquid) are inefficient since the settling rates are very low even with increasing flocculant dosage. Further, turbidity was found to increase with increasing amounts of the above polymers. No settling of particles could be observed with Morfloc A. With Morfloc PG, turbidity of the supernatent slightly increased with flocculant addition. Hyfloc-A was a better flocculant than the above. Morfloc A-100 exhibits steeper settling rates than Morfloc A-30. Increasing concentrations of Caflo N-6 and N-7 decreases turbidity of the supernatent with simultaneous increase in settling rates. With Morfloc A-40H, the settling rate was found to increase steeply with increase in concentration. Still higher dosages, decrease settling rate and increase turbidity. Califloc A and Polyacrylamide (N) were found to be the most effective with respect to both settling rate and increased clarity of the supernatent.

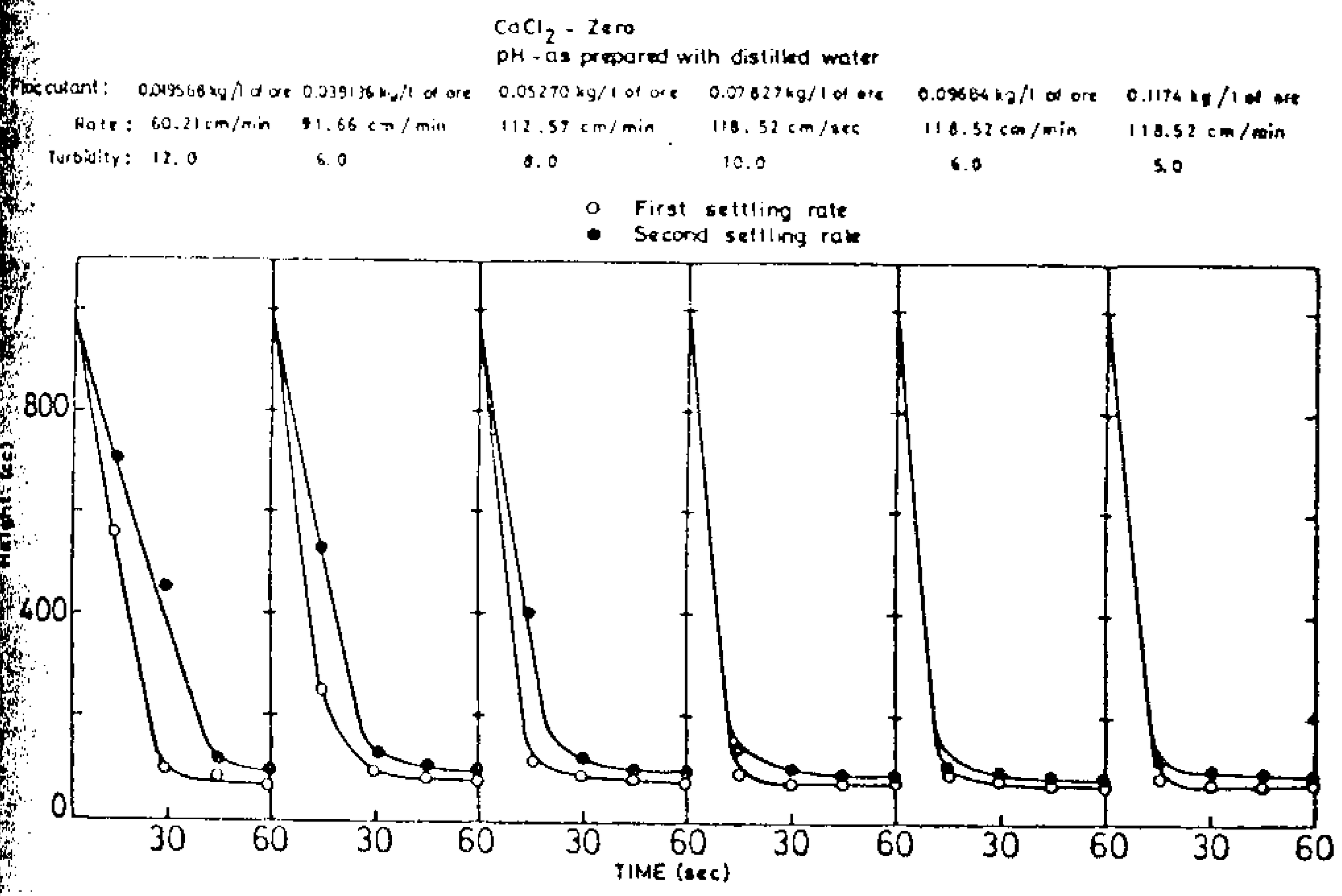


Fig. 1 First and second settling curves for califloc at P.D. of 5%

Califloc was then chosen for a systematic evaluation since its usage resulted in higher settling rate and floc strength when compared to Polyacrylamide (N) for a given concentration. The minimum califloc concentration required to initiate settling was found to be about 0.006 kg/ton.

The effect of addition of calcium chloride at a constant level of the flocculant addition at 5% pulp density at natural pH was then studied. Turbidity was found to decrease with calcium additions.

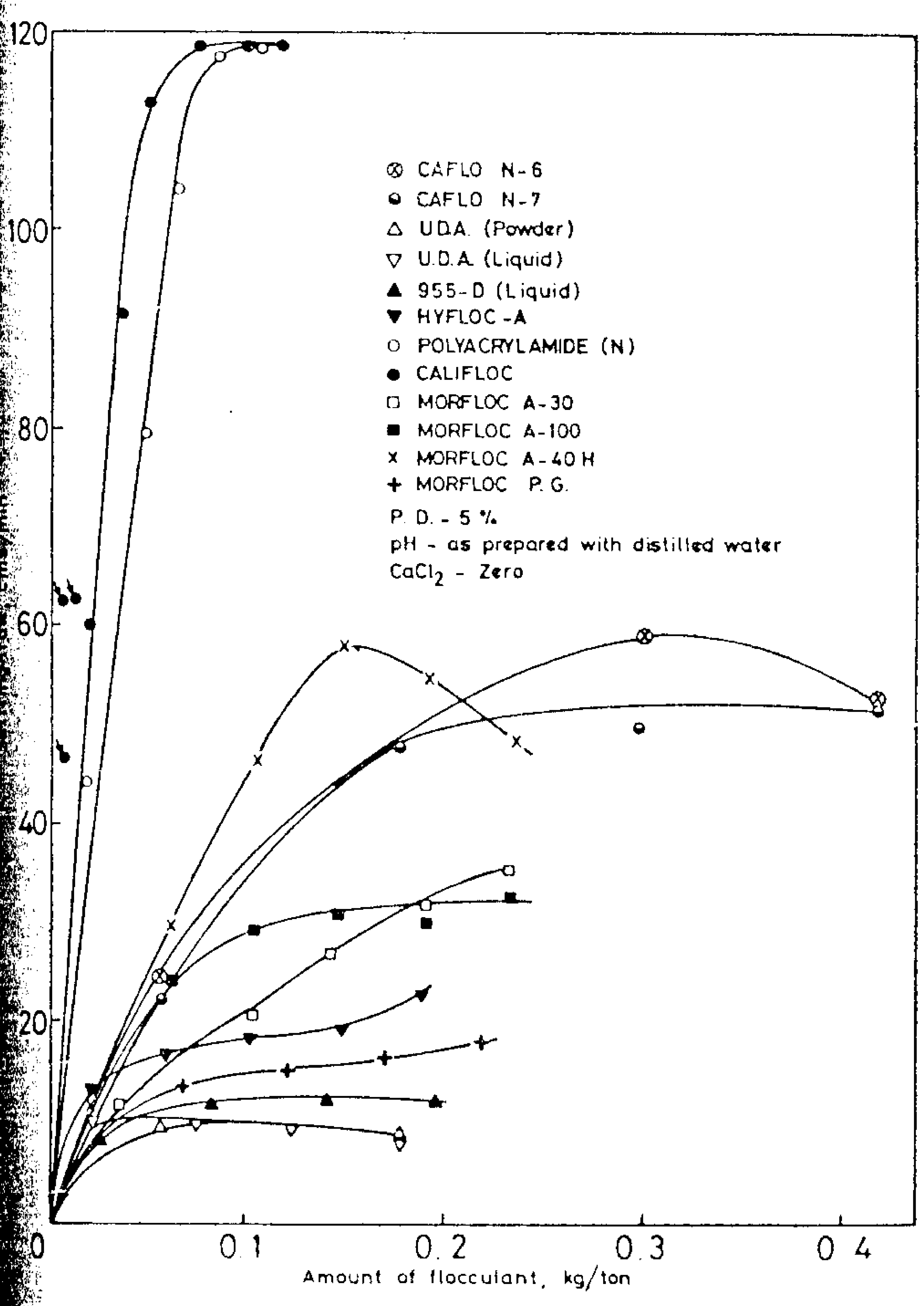


Fig. 2 Settling rate studies with increasing dosage of synthetic polymeric flocculants

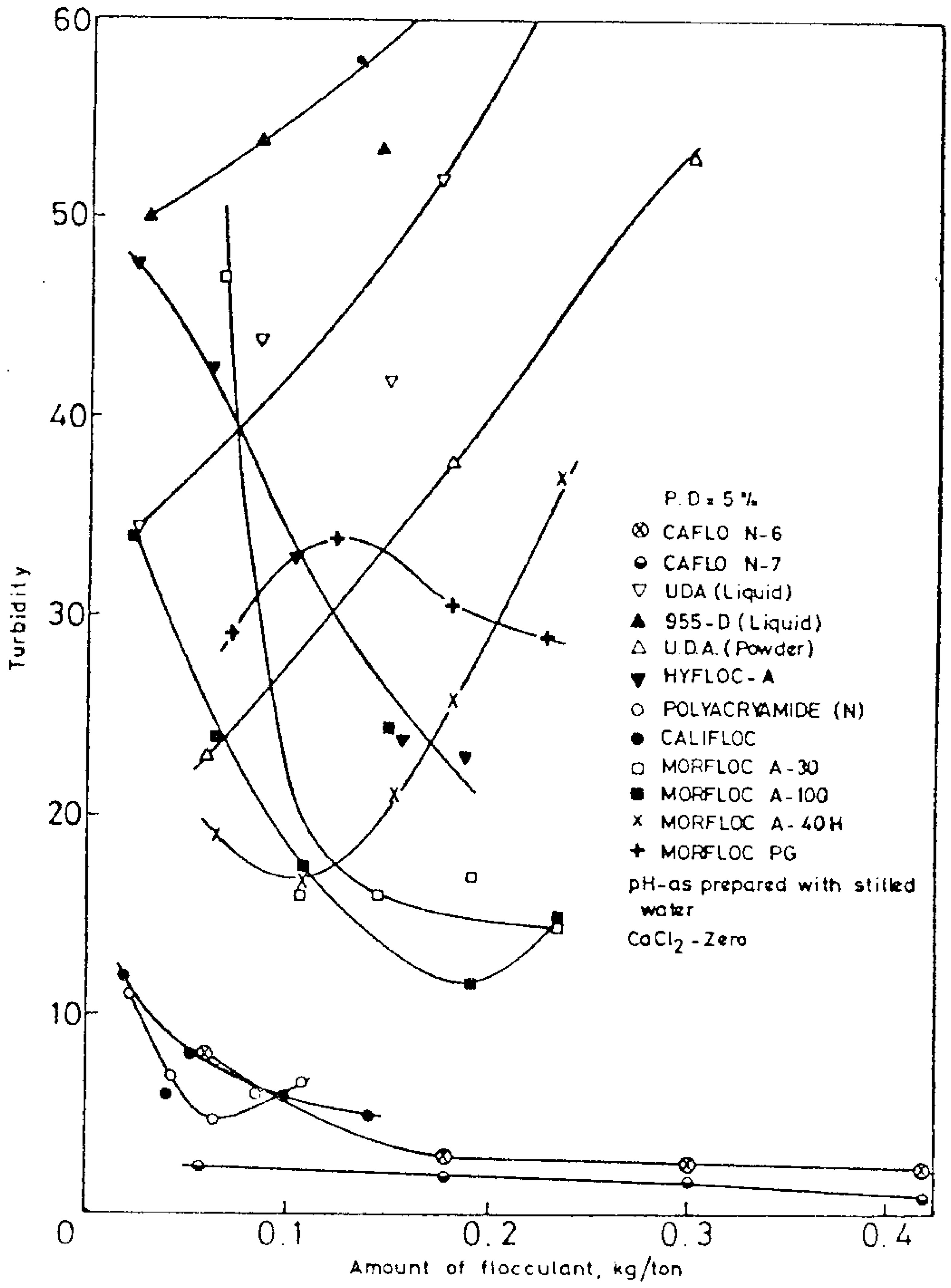


Fig. 3 Turbidity studies with increasing dosage of synthetic polymeric flocculants

Effect of pH on settling rate and turbidity at a constant califloc concentration of 0.012 kg/ton was also separately evaluated at different levels of calcium chloride addition (calcium additions were made only at pH values higher than 10.2). As can be seen from Fig. 4, the settling rate steeply increases with pH upto 4, then decreasing slightly and then remaining at a constant level till pH 8.2. At still higher alkaline values, the settling rate was found to decrease sharply in the absence of calcium chloride additions. Thus calcium additions were found essential at alkaline pH levels to achieve desirable settling rates besides the presence of the flocculant. Turbidity values were found to decrease gradually upto a pH of 4 and then steadily increasing upto pH 8.2 above which it increased still steeply.

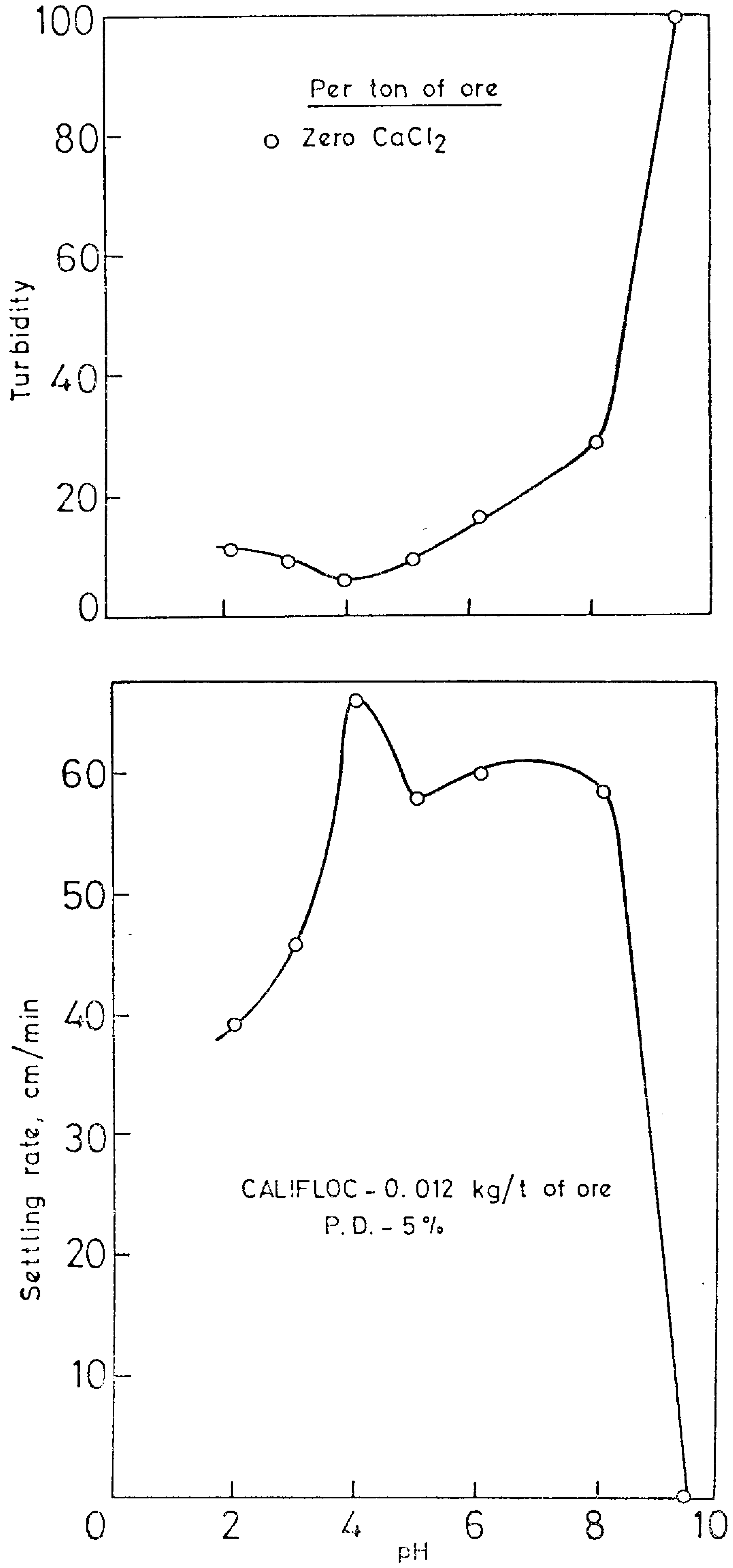


Fig. 4 Settling rate and turbidity variation with varying pH and increasing $CaCl_2$ addition (at higher pH) at constant P.D. and califloc concentration

The effects of sequence of addition of calcium and the flocculant were then tested at pH 12 (for a calcium chloride level of 1.05 kg/ton). From Fig. 5 it could be seen that, when califloc was added first, the settling rate was very low, although increasing flocculant dosages increased the settling rate marginally. The turbidity value, on the otherhand, initially decreased and then increased rapidly with increasing flocculant concentration. Initial additions of calcium chloride on the otherhand, drastically increases the settling rate and sharply decreases the turbidity.

Tests were then carried out by adding increased amounts of calcium chloride at two flocculant levels, namely, 0.006 and 0.06 kg/ton, at pH 12 and the

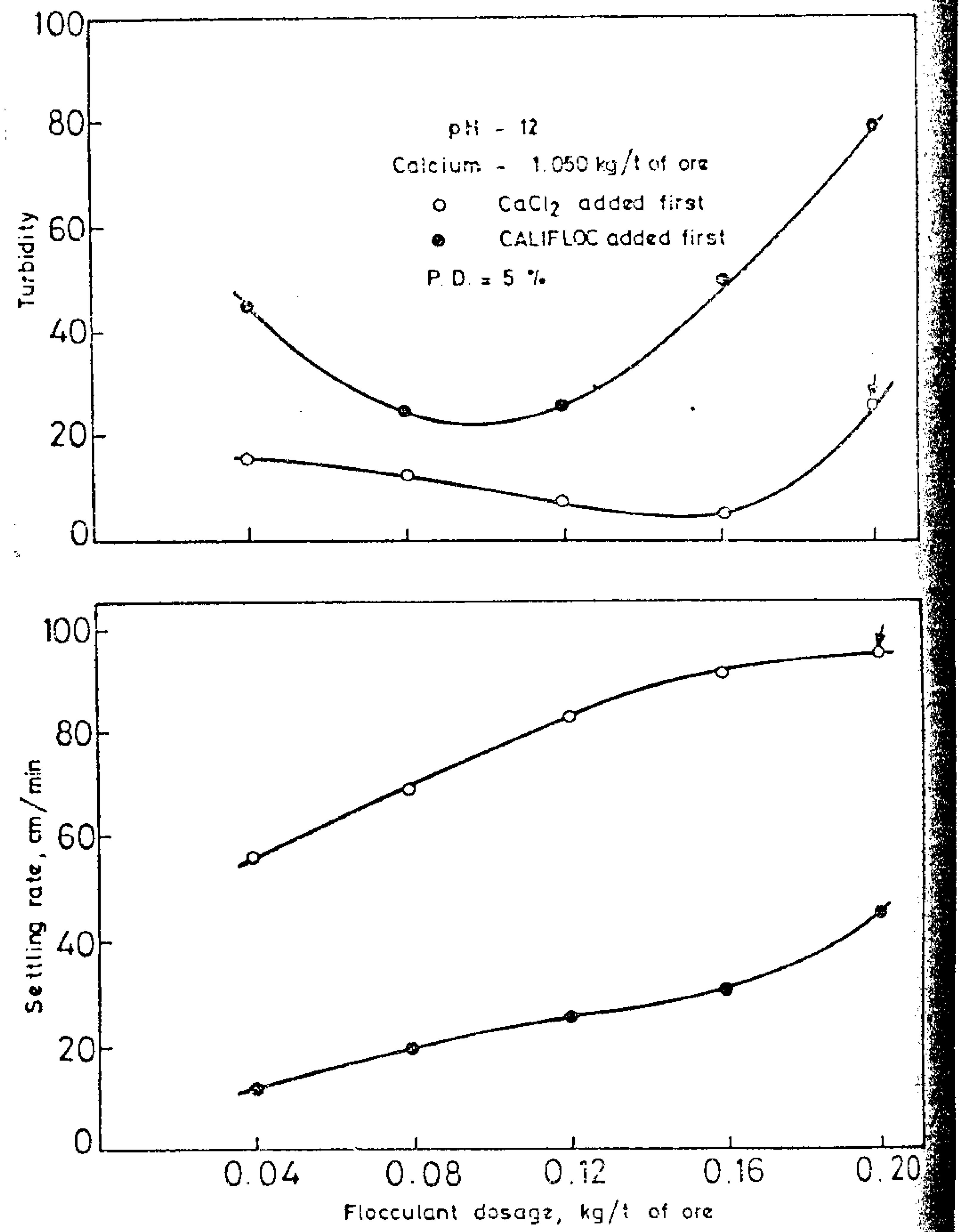


Fig. 5 Settling rate and turbidity variation with increasing dosage of califloc at fixed calcium concentration when order of addition is reversed.

results are shown in Fig. 6. It could be seen that the settling rates at lower flocculant concentrations increase gradually. At higher calcium chloride additions, the trend was towards rapid increase in settling rate. At higher califloc concentration, on the otherhand, the settling rate increased with calcium chloride. At still higher calcium dosages, the settling rate tends to remain constant. Turbidity values increase to 36 when 25 kg/ton of calcium chloride was added, with the formation of $Ca(OH)_2$ precipitate. At higher califloc concentrations, turbidity decreased.

Factorial experiments of 2^3 type as detailed in Tables II and III were then carried out followed by an analysis of variance to find out the main effects and interactions affecting the flocculation process. It was observed that at lower pH range, the settling rate is strongly dependent on the amount of califloc added. The amount of suspended particles in the supernatent depends strongly on pH, califloc and calcium chloride concentrations. At higher pH also, the settling rate is strongly dependent on pH and califloc concentration, calcium concentration and pH are also significant factors. Turbidity, on the otherhand, depends strongly on pH, calcium and califloc concentrations and also on the interaction between calcium and pH, pH and califloc and possibly between calcium and califloc.

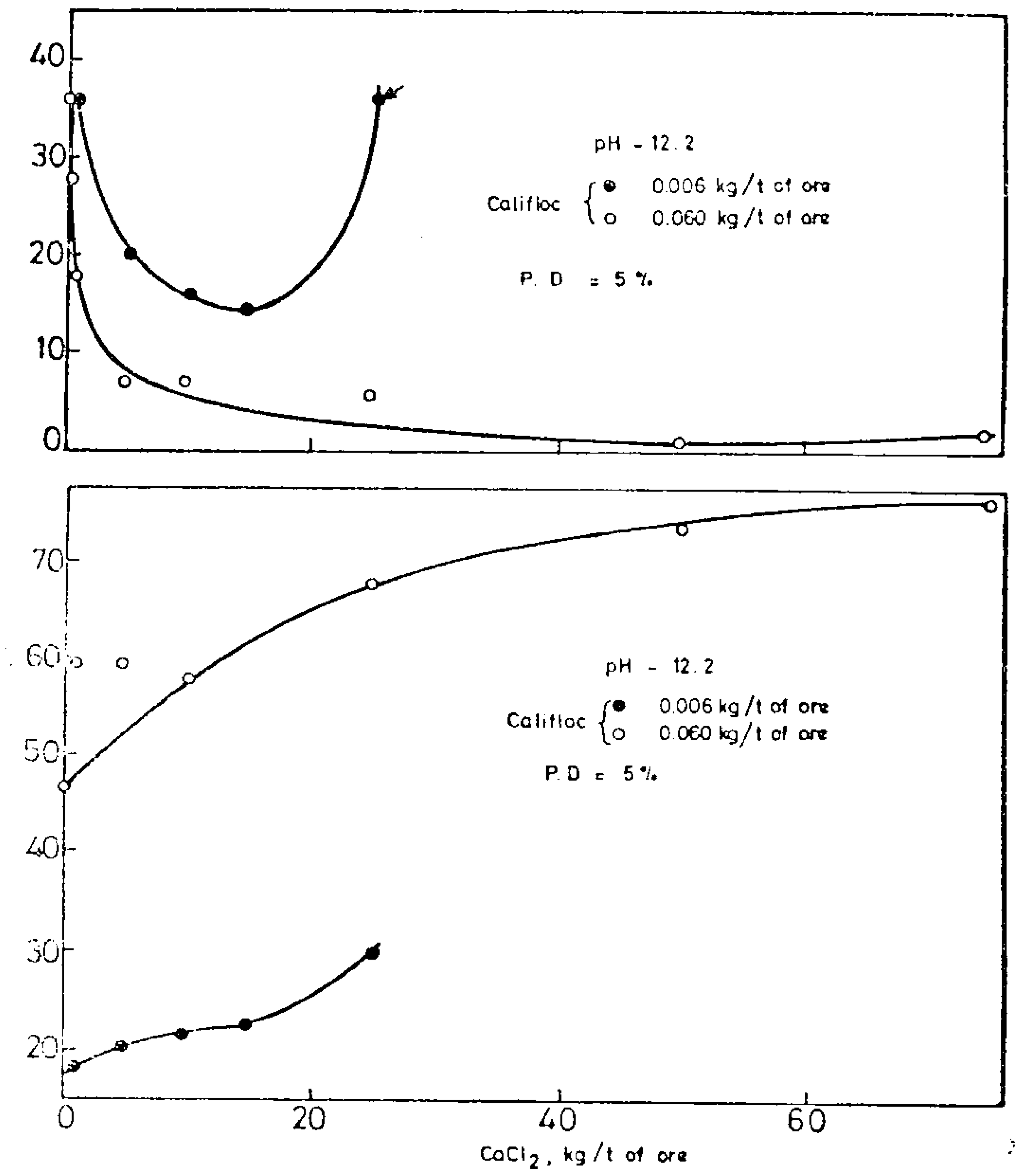


Fig. 6 **Settling rate and turbidity variation with increasing dosage of calcium chloride at lower and higher value of flocculant concentration**

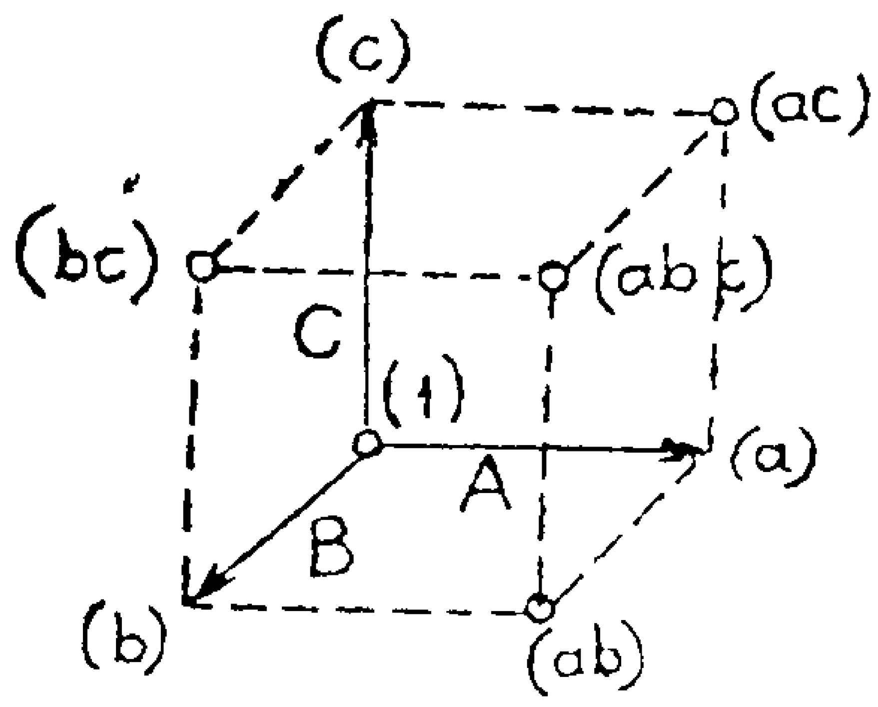
TABLE II—2^3 factorial design (at lower pH level)

Factors

	−	+
A = pH	6	9
B = Calcium kg/ton of ore	0.02596	0.1558
C = Califloc kg/ton of ore	0.006	0.06

Response

Y_1 = Settling rate (cm/min.)
Y_2 = Turbidity
Y_3 = Residual Ca^{++} in 25 ml. of supernatant (mg).



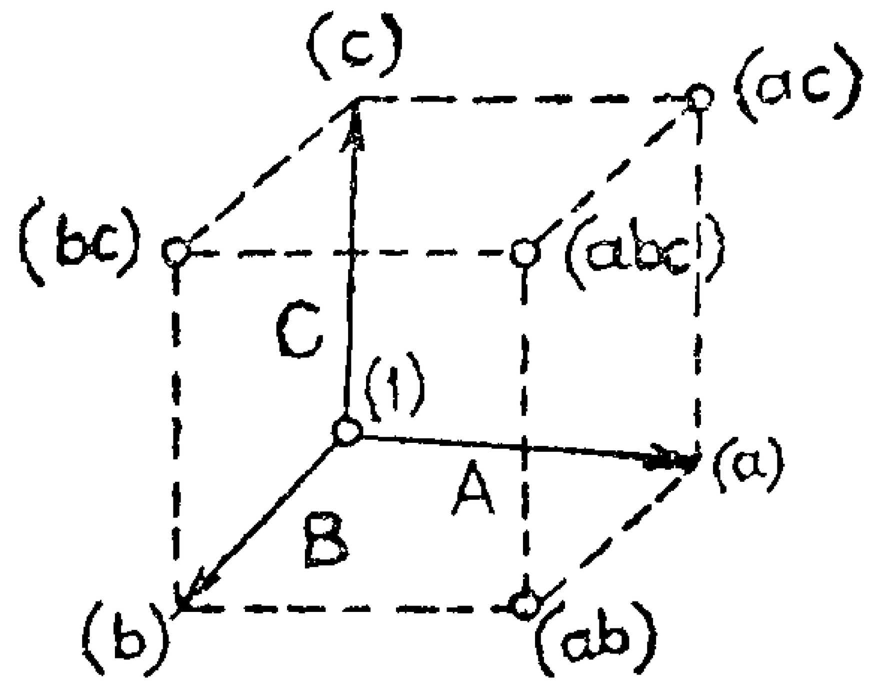
Variation	Factor levels A	Factor levels B	Factor levels C	Responses Y_1	Responses Y_2	Responses Y_3
1	6	0.2596	0.006	48.04	24*	0.076152
a	9	0.2596	0.006	Zero	70*	Zero*
b	6	1.5594	0.006	52.36	16*	0.214428*
ab	9	1.5594	0.006	60.38	50*	0.024048+
c	6	0.2596	0.06	118.52*	4*	0.06012
ac	9	0.2596	0.06	119.78	50*	Zero
bc	6	1.5594	0.06	108.32+	4+	0.21522
abc	9	1.5594	0.06	98.77	14*	Zero
Repeat test						
abc	9	1.5594	0.06	99.82	10	0.036072
				91.90	10	0.0501
				108.32	11	0.072144
				112.88	10	0.036072
				91.41	9	0.052104
				108.32	8.5	0.008016

+possibly significant for 95% confidence limit.
*denotes high significance of factor/interaction.

TABLE III—2^3 factorial design (at higher pH level)

Factors

	−	+
A = pH	9	12
B = Calcium kg/ton of ore	0.1558	1.0388
C = Califloc kg/ton of ore	0.006	0.06



Response
Y_1 = Settling rate (cm/min)
Y_2 = Turbidity
Y_3 = Residual C_a^{++} in 25 ml of supernatant (mg).

Variation	Factor levels A	B	C	Responses Y_1	Y_2	Y_3
1	9	1.5594	0.006	60.38	50*	0.024048*
a	12	1.5594	0.006	17.36*	70*	Zero*
b	9	10.388	0.006	40.04+	27*	1.1022*
ab	12	10.388	0.006	21.71+	2*	Zero*
c	9	1.5594	0.06	98.77*	14*	Zero*
ac	12	1.5594	0.06	63.38	50*	Zero*
bc	9	10.388	0.06	74.87	4+	1.2224*
abc	12	10.388	0.06	59.26	2+	Zero*
Repeat test						
abc	12	10.388	0.06	56.59	3	Zero
				69.72	2	Zero
				64.07	4	Zero
				56.44	5.5	Zero
				58.78	2.5	Zero
				59.26	3.5	Zero

* highly significant for 95% confidence limit.
+possibly significant for 95% confidence limit.

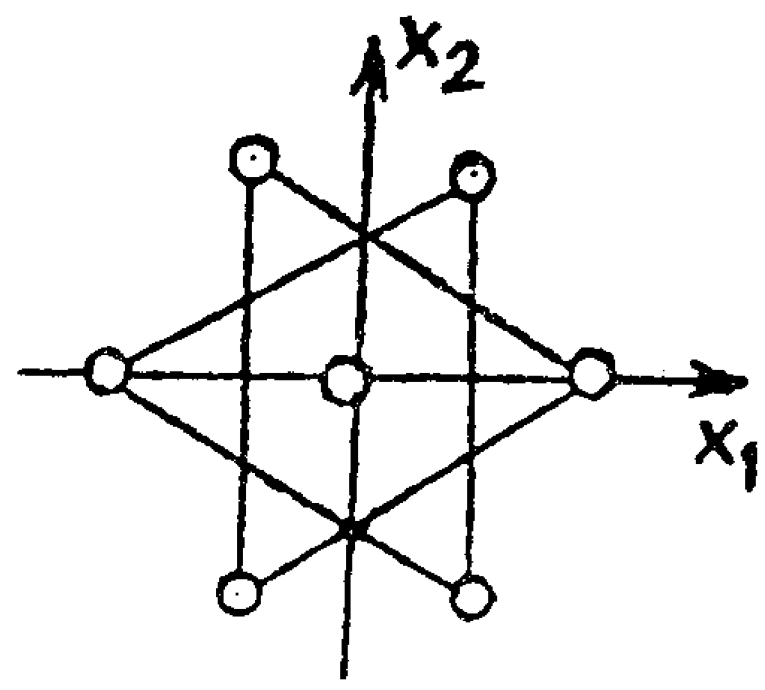
TABLE IV—Hexagonal design and response data for varying pH at lower range and zero calcium concentration

Factor Range :

pH = 6 – 8

Flocculant (califloc) = 0.01522 – 0.0568 kg/ton of ore.

Calcium concentration = zero.



Responses :
Y_1 = Settling rate (cm/min.)
Y_2 = Turbidity

Design level X_1	X_2	Factor level pH before floccula-tion	pH after floccula-tion	Flocculant conc.	Responses Y_1	Y_2
1.000	0.0	8.0	7.55	0.036	77.32	80
0.500	0.866	7.5	7.5	0.0568	117.89	50
– 0.500	0.866	6.5	6.7	0.0568	106.88	19
– 1.00	0.0	6.0	6.45	0.036	81.74	9
– 0.500	–0.866	6.5	6.5	0.01522	47.16	16.5
0.500	–0.866	7.5	7.5	0.01522	42.18	50
0.0	0.0	7.0	7.0	0.036	77.75	18
0.0	0.0	7.0	7.1	0.036	85.11	28
1.0	0.0	8.0	7.5	0.036	74.47	80
– 1.0	0.0	6.0	6.2	0.036	78.80	11

Code $X_1 = pH - 7$; Code $X_2 = \frac{F - 0.036}{0.024}$

three separate orthogonal hexagonal designs—two at lower pH levels and one at higher pH level were then formulated at illustrated in Tables IV to VI. Based on such hexagonal designs, regression equations were developed to equate settling rate and turbidity with the variables. Response contours were then plotted for two responses ; namely, settling rate and turbidity as a function of the variables as illustrated in Figs. 7 to 12.

Figure 7 shows the surface contours for settling rate. The nature of the above surface contours indicate that both pH and califloc concentration play an important role in bringing about higher settling rate. Upto about 0.04 kg/ton of the flocculant, for attaining a similar settling rate, higher amount of califloc are to be used with increasing pH. In other words, from an economical view point also, it is preferable to maintain lower pH at which only smaller concentrations of califloc is needed, to achieve similar settling rates as at higher pH. However, there is a change in the nature of the response surfaces for higher califloc concentrations (above 0.04 kg/ton). In this case, the amount of the califloc required to achieve a similar settling rate increases with decrease in pH, with a minimum point at around pH 7 to 8 ; again showing a slight increasing trend at higher pH.

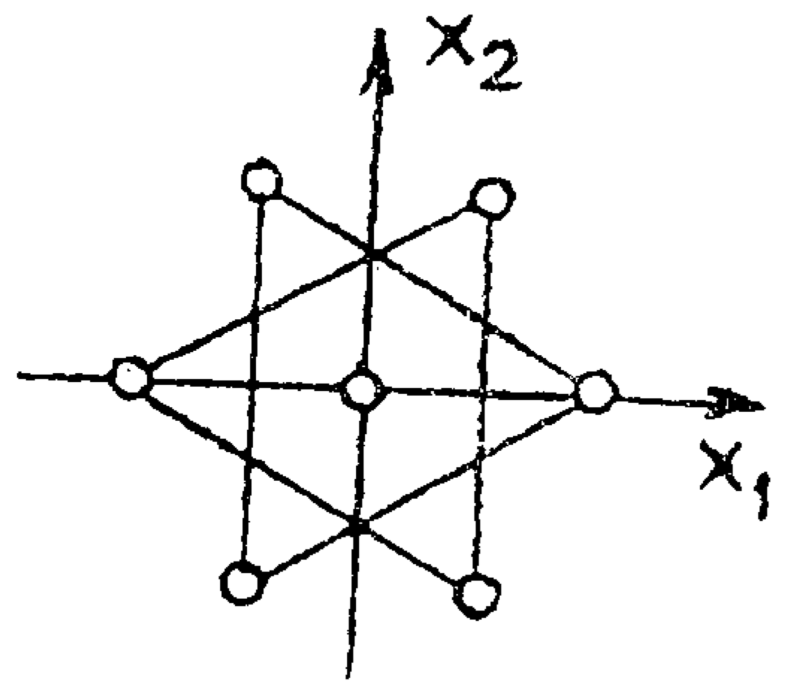
The above response contours have to be compared with those obtained in the presence of a fixed calcium concentration (0.06 kg/ton) (Fig. 9). The response surface show a similar pattern throughout with respect to settling rate as a function of califloc concentration and pH, unlike the ones for above case. Settling rate increases with increase in califloc concentration. However, there is a pH region around 7 at which the califloc concentration required, to attain a desired settling rate, is minimum. In general, the amount of califloc required to get the desired response decreases with pH upto about 7 and then increases.

The effect of calcium, however, becomes significant with respect to turbidity as has already been brought out. Response contours for turbidity in the presence and absence of calcium in the pH range of 4 to 8 are given in Figs. 8 and 10. In the absence of calcium, better clarity of supernatant could be achieved in the pH range of 5 to 7. The effect of califloc concentration is increasingly felt only in the above pH ranges, and it appears as though turbidity becomes independent of

TABLE V—Hexagonal design and response data for varying pH at lower range and fixed calcium concentration

Factors :
pH = 6 – 8
Flocculant (califloc) = 0.01522 – 0.0568 kg/ton of ore.
Calcium concentration (fixed) = 0.0525 kg/ton of ore.

Responses :
Y_1 = Settling rate (cm/min)
Y_2 = Turbidity
Y_3 = Residual calcium = zero.



Design level		Factor level			Responses	
X_1	X_2	pH before floccula-tion	pH after floccula-tion	Flocculant conc.	Y_1	Y_2
1.000	0.0	8.0	7.5	0.036	76.06	14
0.500	0.866	7.5	7.4	0.0568	106.59	10
– 0.500	0.866	6.5	7.0	0.0568	102.79	4
– 1.000	0.0	6.0	6.5	0.036	79.01	6
– 0.500	–0.866	6.5	6.7	0.01522	48.99	12
0.500	– 0.866	7.5	7.5	0.01522	51.53	14
0	0	7.0	6.95	0.036	84.88	10
0	0	7.0	6.8	0.036	79.01	9
1.0	0	8.0	7.85	0.036	79.01	12.5
– 1.0	0	6.0	6.3	0.036	78.38	6.0

$$\text{Code } X_1 = \frac{pH - 7}{1} ; \quad \text{Code } X_2 = \frac{F - 0.0036}{0.0024}$$

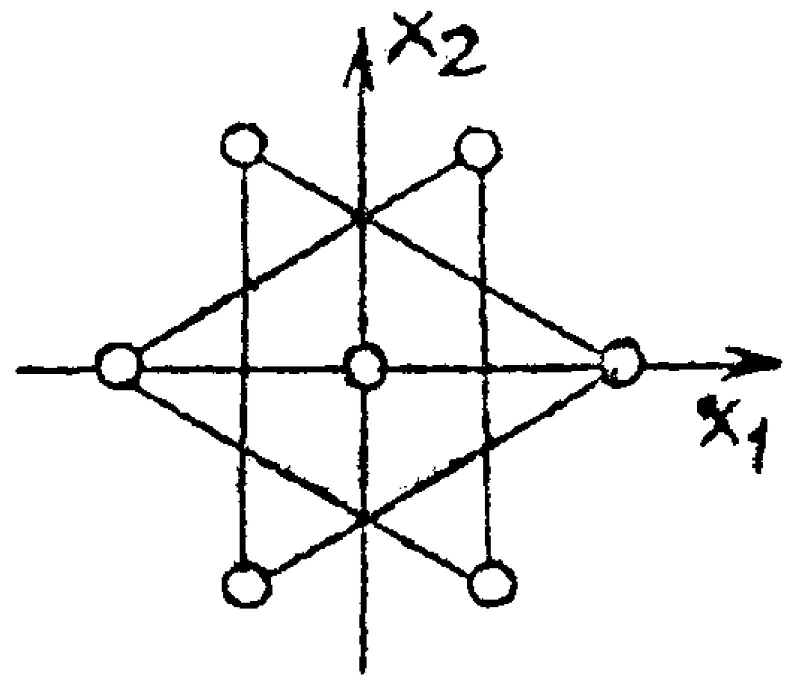
TABLE VI—Hexagonal design and response data for fixed pH 12 and varying calcium and califloc concentration

Factors :

pH (fixed) = 12
Flocculant (califloc) = 0.0136 – 0.0344 kg/ton of ore.
·Calcium = 1.04 – 2.08 kg/ton of ore

Responses :

Y_1 = Settling rate (cm/min)
Y_2 = Turbidity
Y_3 = Residual calcium = zero.



Design level		Factor level		Response	
X_1	X_2	Calcium	Flocculant	Y_1	Y_2
1.000	0	2.08	0.024	56.74	15.0
0.500	0.866	1.82	0.0344	56.14	12.5
– 0.500	0.866	1.30	0.0344	59.29	6.5
– 1.000	0.0	1.04	0.024	57.95	19.0
– 0.500	– 0.866	1.30	0.0136	37.42	14.0
– 0.500	– 0.866	1.80	0.0136	36.94	12.0
0.0	0.0	1.56	0.024	55.42	14.0
0.0	0.0	1.56	0.024	53.59	12.0
1.0	0.0	2.08	0.024	58.28	14.5
– 1.0	0.0	1.04	0.024	57.04	23.5

$$\text{Code } X_1 = \frac{\text{Calcium} - 1.56}{0.52} \quad \text{i.e. } 0.52\ X_1 + 1.56 = \text{Calcium.}$$

$$\text{Code } X_2 = \frac{\text{Flocculant} - 0.024}{0.012} \quad \text{i.e. } 0.012\ X_2 + 0.024 = \text{Floccu ant}$$

califloc concentration at higher pH (though a similar trend has been observed toward acidic pH, no special mention of the same has been made here as these regions were arrived through extrapolation).

The contribution from calcium additions can be seen in the light of widening of pH range for obtaining acceptable levels of clarity for the supernatant for a given califloc concentration. However, the clarity further improves with increasing dosage of califloc at fixed calcium concentration in the pH range 5 to 7.

As has been mentioned earlier, the effect of calcium additions becomes highly significant only in the high alkaline regions. Response contours for settling rate and turbidity for a fixed pH of 12, with varying calcium and califloc concentrations are given in Figs. 11 and 12.

The role of calcium at this high alkaline pH appears to be a bit complex. As has already been established, the interaction between calcium and pH on the one hand and that of calcium and califloc on the otherhand are highly significant. The results with respect to settling rate and turbidity hence, have to be interpreted with the above knowledge. In the clarification of mineral suspensions, calrity of the supernatant is a more important aspect than settling rate. Though one would accept higher settling rate coupled with increased clarity as the desired condition, there are exceptions to such a role. It would, therefore, be better to look for maximum clarity coupled with "acceptable settling rate", which need not be the maximum. To achieve the above combination, it is essential to maintain the califloc and calcium concentrations at optimum levels, especially at highly alkaline pH. This fact is clearly reflected in Fig. 12. With respect to good clarity of the supernatant, a calcium concentration in the range of 1.5—2.5 kg/ton may be desirable. It is also observed that the effective calcium concentration could be brought down with successive increase in califloc concentration and vice-versa. Higher concentrations of calcium (higher than 2.5 kg/ton) is not desirable since turbidity was found to increase due to hydrolysis of calcium ions. Increasing amount of califloc and calcium would increase the settling rate. But, it would be preferable to keep calcium concentrations at lower levels with a view to achieve better clarity also.

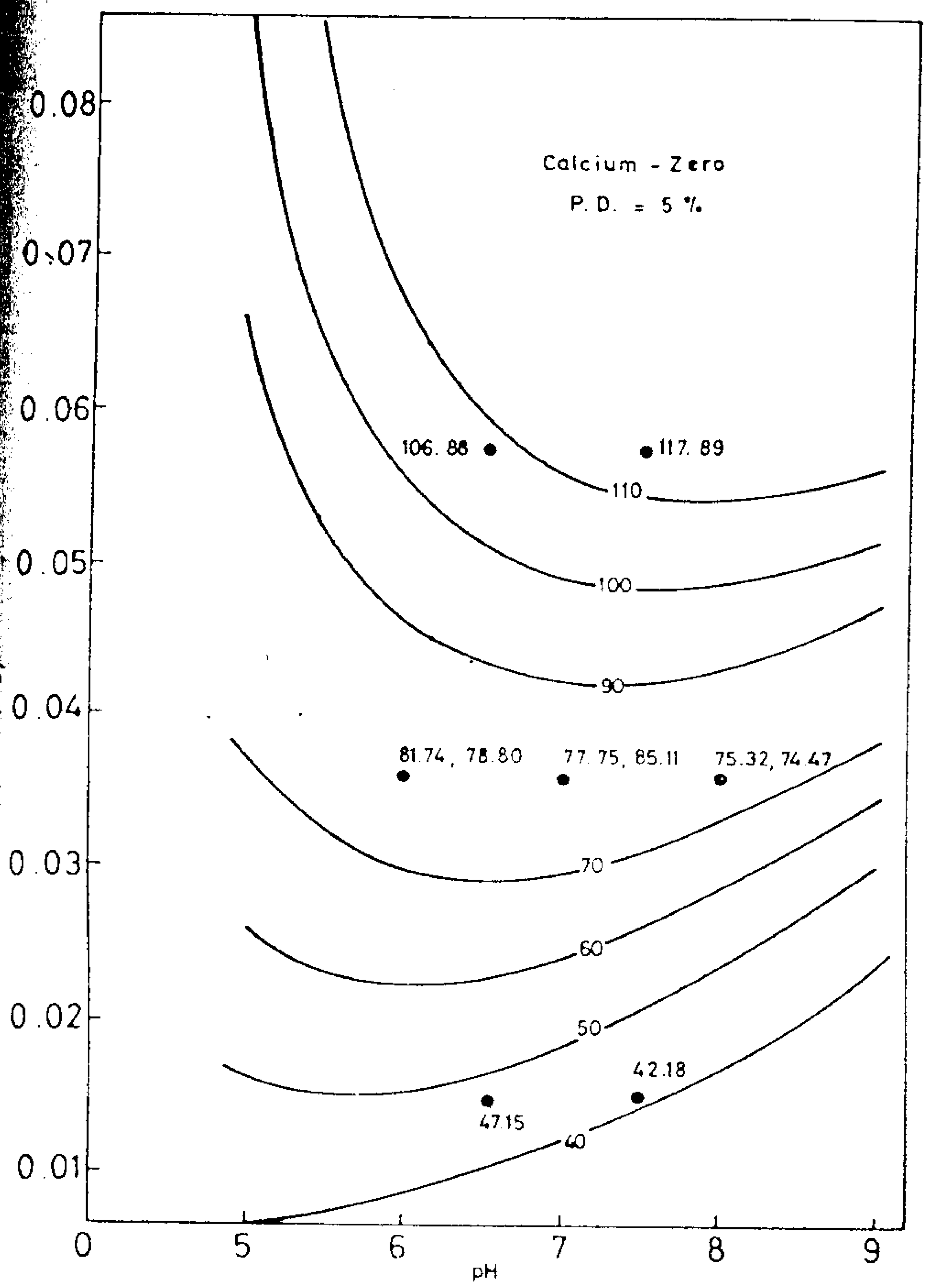


Fig. 7 Response contours for settling rates with varying pH and califloc concentration only

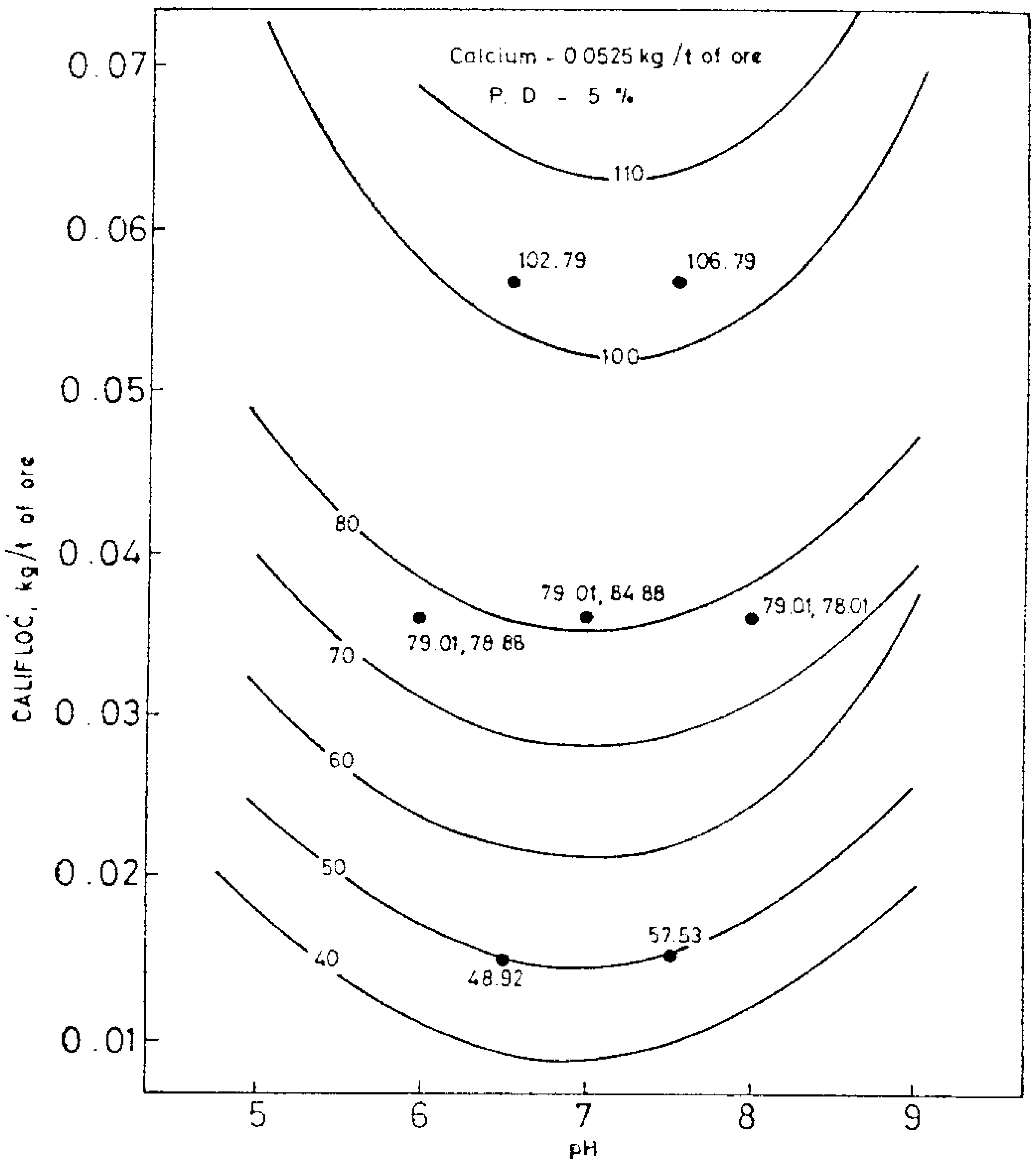


Fig. 9 Response contours for settling rates with fixed calcium concentration and varying pH and califloc concentration

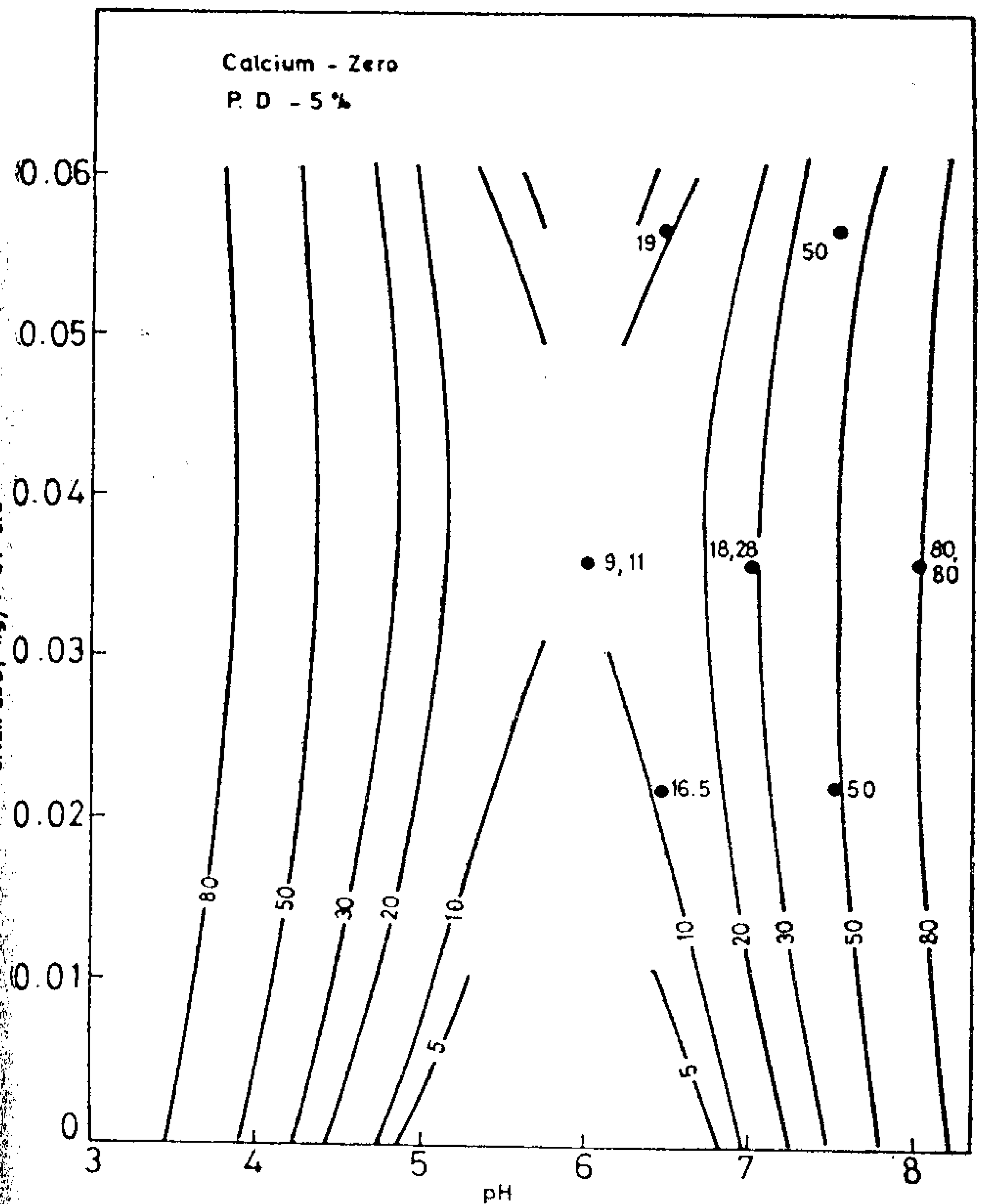


Fig. 8 Response contours for turbidity with varying pH and califloc concentration only

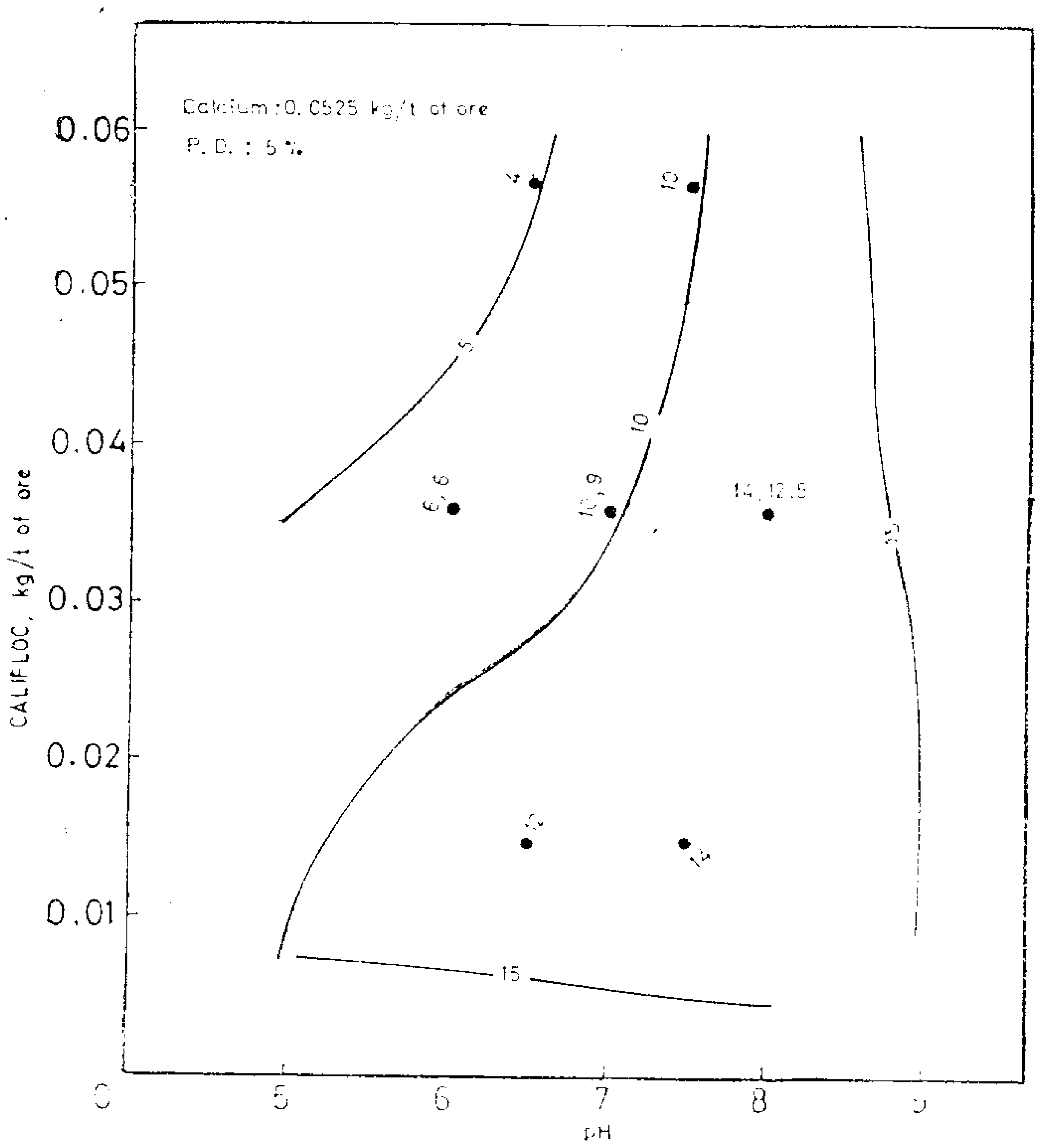


Fig. 10 Response contours for turbidity with fixed calcium concentration and varying pH and califloc concentration

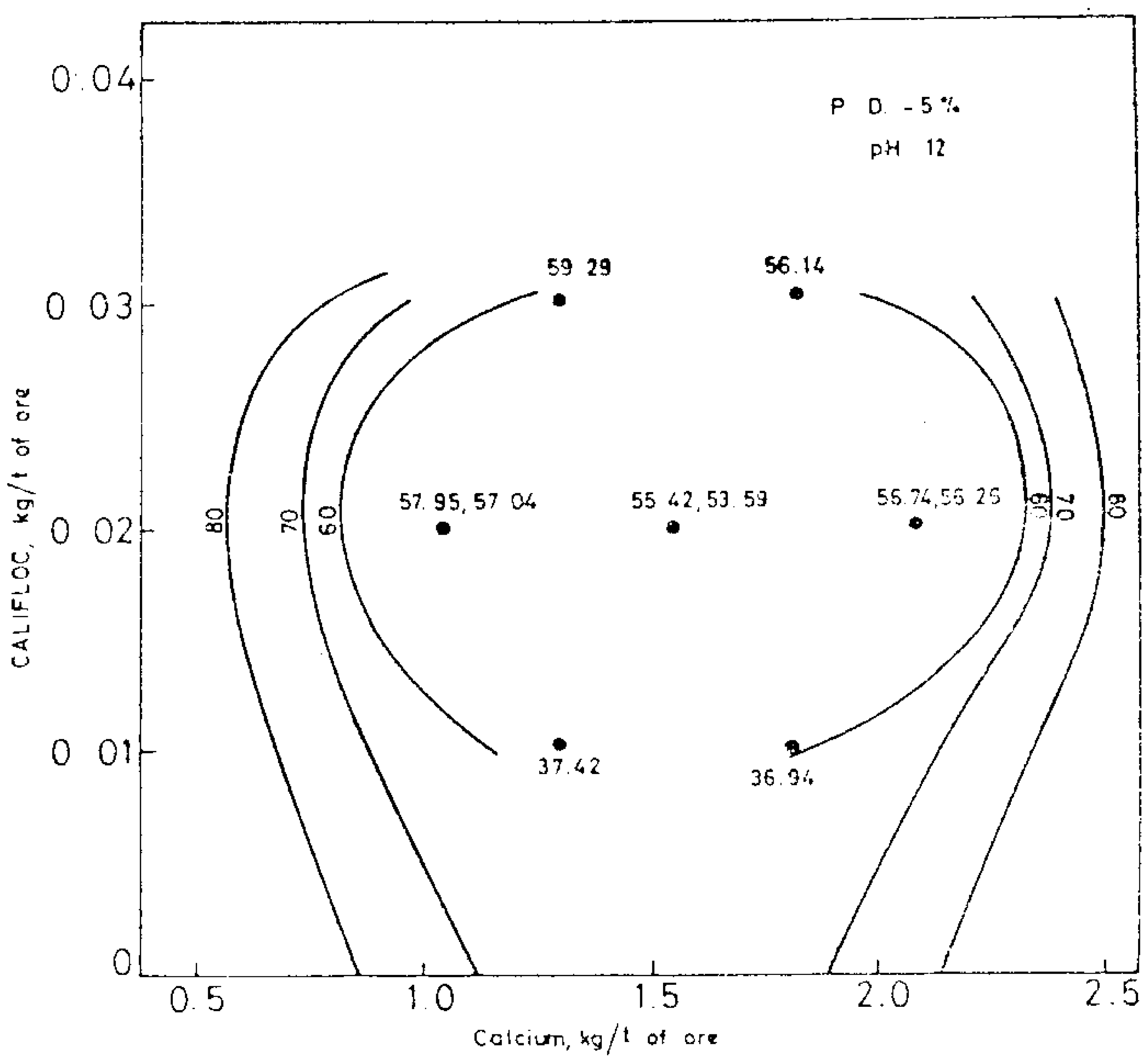


Fig. 11 Response contours for settling rate at fixed pH 12 and varying califloc and calcium concentration.

Experiments carried out at pH 12 on sequence of additions of calcium and califloc indicate the effect of calcium-califloc interaction as well as the effect of calcium additions on the surface charge of haematite at alkaline pH. Addition of calcium brings about its strong interaction with the media, resulting in the formation of $CaOH^+$ which then aids in decreasing or reversing the surface charge. Subsequent califloc addition facilitates stronger electrostatic and hydrogen-bonding between the modified haematite surface and the flocculant, resulting in higher settling rate and lower turbidity. A reversal in the above sequence of addition, on the otherhand, would not bring about the desired results.

CONCLUSIONS

The following conclusions could be arrived at based on this work.

1. Califloc is one of the flocculants for Donimalai iron ore fines.

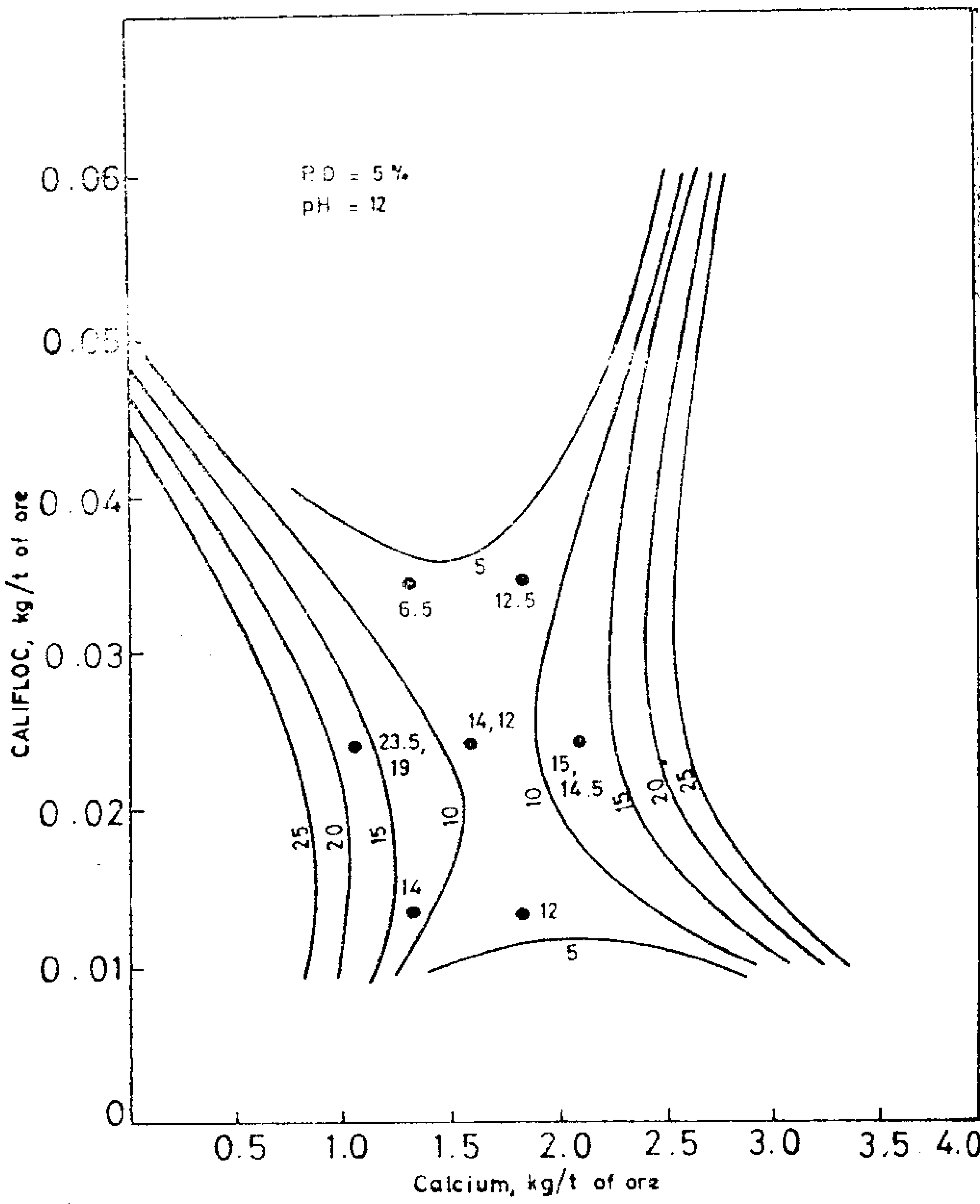


Fig. 12 Response contours for turbidity at fixed pH and varying califloc and calcium concentration

2. Additions of calcium chloride improves settling rate and clarity significantly at alkaline pH values; whereas at acidic levels no addition of calcium is necessary to achieve flocculation.
3. The sequence in which calcium and the flocculant are added is an important factor in deciding the efficiency of flocculation.
4. At higher pH, there exists a strong interaction between added calcium and the califloc flocculant.
5. Statistically designed experiments bring out the important main factors and interactions affecting the flocculation process.