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# Identification of Soil-Water Chemical Parameters for the Prediction and Treatment of Suspended Solids in Surface Water Reservoirs of Coal Mine Lands

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IDENTIFICATION OF SOIL-WATER CHEMICAL PARAMETERS FOR THE PREDICTION AND  
TREATMENT OF SUSPENDED SOLIDS IN SURFACE WATER RESERVOIRS OF COAL MINE LANDS

By

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## ABSTRACT

High concentrations of suspended solids in coal mine sedimentation ponds are a factor in lowering water quality. Colloidal particle settling simulations were carried out in the laboratory to test the influence pH and dissolved solids have on concentration and settling rates of suspended solids. The results of the study reveal that the pH range of colloidal coflocculation for the samples tested is between 3.5 and 4.5. Furthermore, liming simulation of acidic sediments, as expected increased colloid dispersion. This increase was dependent on the magnitude of the sodium adsorption ratio (SAR). The greater SAR systems maintained a greater concentration of colloidal suspended particles. However, for the same SAR value when the ionic strength was increased from 4 meq L<sup>-1</sup> to 8 meq L<sup>-1</sup>, sedimentation rate of colloidal particles decreased. The data also show evidence that for the same SAR values when substituting magnesium for calcium, the rate of particle settling increased for one sample but decreased for another. This unexpected behavior is under further investigation.

DESCRIPTORS: Suspended Solids; Sedimentation; Sedimentary Basins; Spoil Disposal; Water Quality; Colloids; sodium adsorption ratios; Clay Minerals.

IDENTIFIERS: Spoil Water; Coal Mine Sedimentation Ponds.

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## CHAPTER I INTRODUCTION

The objectives of the study were:

1. Determine the pH of coflocculation, for randomly selected samples, by employing standard potentiometric titrations.
2. Evaluate the influence of sodium adsorption ratio (SAR), pH and ionic strength on the rate of colloidal particle settling.
3. Evaluate the influence of the SAR and pH interaction, and SAR and ionic strength interaction on the rate of colloidal particle settling.

Sediment generation from land distributed for commercial development and/or surface mining of coal is a major problem for several reasons including: a) its potential to silt out stream channels, rivers, lakes and reservoirs, b) clay size solids in suspension are pollutants since they inhibit aquatic life and c) suspended clay sediments will have to be removed from the water before it can be used for domestic purposes.

At present, the method of eliminating sediment from water is to estimate the size of the watershed and the maximum amount of sediment to be produced upon disturbance, and then build a sediment pond at the base of the watershed so that the water released meets certain sediment criteria. However, even utilizing the most sophisticated computer model available in designing a pond for maximum trapping efficiency of 99%, the water leaving the pond could have a sediment concentration as high as 10,000 parts per million. Needless to say, water with 10,000 parts per million suspended solids is highly polluted. The reason for this discrepancy between sediment pond trapping efficiency models and actual sediment pond trapping efficiency is that so far computer simulation models do not consider chemical interactions between clay minerals and water.

The proposed research is directed specifically at the problems of clay removal from water. First, it will deal with the causes of high suspended solid loads and then propose mechanisms of removal of suspended clays with minimal changes in water chemistry.

This investigation deals with determining the possible role of the dissolved constituents in controlling clay colloid dispersion and/or flocculation, and furthermore, the influence pH exerts on the settling rates of colloidal suspended particles.

## CHAPTER II-RESEARCH PROCEDURES

### Sample Selection and Analytical Techniques

To meet the objectives of the study, water samples from sedimentation ponds and spoil and/or geologic strata samples representing Eastern and Western Kentucky mine fields were obtained. The water samples were filtered through a Whatman filter No. 42 and then analyzed for Ca, Mg, Na, K, Mn, Fe, by atomic absorption, for Al by colorimetry, for Cl by chloridometry, for  $SO_4$  by turbidometry, for  $HCO_3$  by automatic titrimetry, and for electrical conductivity (EC) with a Markson EC meter, equipped with a flow through electrode and the pH was taken with a combination electrode.

The spoil samples underwent extensive testing, including determination of exchangeable and solution cations at 1:2 spoil-water ratio, pH, electrical conductance, and cation exchange capacity (CEC). Exchangeable cations and CEC determinations were made using N ammonium acetate pH 7 with the procedures described in Black (1965). Particle size determination and mineralogical analysis were carried out by elutriation and X-ray diffraction, respectively. Detailed information on these samples is given in research report No 150 (Evangelou et. al. 1984).

### Experimental Theory

Colloid dispersion and flocculation are multifaceted phenomena. Stum and O'Melia (1968) described control of these processes by double layer swelling, adsorbable species (hydrolyzed iron and aluminum) and chemical bridging. Since the colloids of coal mine sedimentation ponds are most probably mineralogically heterogeneous, both double layer swelling and flocculation by adsorbed hydrolyzable cations may be operative at the same time. The double layer theory considers the clay particle as a flat surface

with a uniformly distributed surface charge and an unequal distribution of counter ions, hence a "double layer". The double layer thickness (DLT) is considered to be approximately the distance from the clay surface to the vicinity of the bulk solution.

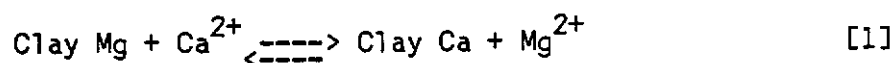
The distribution of the ions near the surface of the clay particle is a function of many parameters. These parameters involve valency of the ions, type of ions, concentration and surface potential. (Van Olphen, 1971; Golst, 1977). Clay minerals that exhibit exchange capacity exhibit a surface electrical potential (Stumm and Morgan, 1970). Ideally there are two kinds of clays in terms of the electric double layer, those that have a constant surface charge and variable surface potential and those that have a constant surface potential and a variable charge. Since clays in soils are a highly heterogeneous mixture, it is impossible to classify them ideally. However one thing is certain, shale clays are mainly dominated by kaolinite and such clays have more of a variable surface charge than they do a variable surface potential. This surface potential decays exponentially and it is controlled by the salt concentration in the solution. The surface potential as modified by the solution chemistry is an approximation of the repulsive force applied to two approaching clay particles in a solution. When two particles collide in a solution system, whether or not the collision will lead to a physico-chemical bond formation between the clay particles (formation of floccules) depends on the net interaction between the repulsive forces of the electric double layers and the attractive forces (so called London-van der Waals forces). The latter are usually only dependent on the distance separating the two particles (Stumm and Morgan 1970).

It is apparent, therefore, that the surface charge density or CEC, along with the electrolyte or salt concentration control the surface potential,

which in turn determines (to a great extent) how close two particles will come during a collision. The extent of influence of the clay surface potential can also be greatly modified by the type of ions within the double layer and not just by the concentration of the bulk solution alone. The relative amounts of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  that will suppress the double layer thickness to the same level are approximately 100, 2, and 0.04 for these ions respectively. The explanation for such a difference is the force by which the clay negative charge attracts these ions. Aluminum is strongly preferred by the clay, compressing the double layer to a minimum, which causes a large number of successful clay particle collisions (leading to physico-chemical bonding among the particles). On the other hand sodium is least preferred, causing a large diffuse double layer, leading to unsuccessful clay particle collisions. In sediment ponds at a relatively high pH, aluminum has precipitated leaving a Ca, Mg, Na mixture. It is apparent that for a particular clay system two factors would dictate the degree of successful collisions (causing flocculation). One is the selective preference of cations by the clay charge sites and the second is the overall salt concentration in the system.

In general, clays prefer trivalent cations over divalent and divalent cations over monovalent. Within a similar valency, clays show preference for the cation with the smaller hydrated radius. Examples of the above statements are as follows: Clays prefer  $\text{Al}^{3+}$  over  $\text{Ca}^{2+}$  and  $\text{Ca}^{2+}$  over  $\text{Na}^+$  because of the valency effect and  $\text{K}^+$  over  $\text{Na}^+$  because  $\text{K}^+$  has a smaller hydrated radius than  $\text{Na}^+$ .

We can expressed exchange phenomena mathematically as follows:



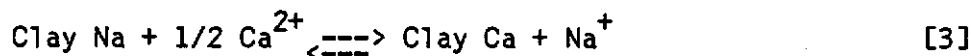
Rearranging:

$$K_{Mg}^{Ca} = \frac{ClayCa (Mg^{2+})}{ClayMg (Ca^{2+})} \quad [2]$$

where  $K_{Mg}^{Ca}$  is the "selectivity coefficient" and Clayx and (x) denote exchangeable and solution cations in meq/100 grams and mmol/l<sup>-1</sup> respectively. A  $K_{Mg}^{Ca}$  greater than 1 indicates preference for Ca, whereas a

$K_{Mg}^{Ca}$  equal to 1 shows no preference (Hunsaker and Pratt, 1971).

Selectivity is a very important point to consider as we shall see later in this section. Soils in general show a  $K_{Mg}^{Ca}$  value of near 1, which indicates that calcium and magnesium should behave similarly in terms of causing dispersion of clay. However, there are certain well established exceptions. Vermiculite, for example, shows a greater preference for magnesium. Organic matter shows a greater preference for calcium. Under such circumstances, in relatively dilute calcium-magnesium sediment pond water, the degree of dispersion becomes a matter of which of the two ions dominates the system and what type of clay particle is present. Another expression that is often used to describe an exchange reaction between a monovalent and a divalent cation as in this case between sodium and calcium is:



Rearranging:

$$K_{Na}^{Ca} = \frac{ClayCa (Na)}{Clay Na (Ca^{2+})} 1/2 \quad [4]$$

where clayX is in meq/100 grams and (X) is mmol/l in solution. Assuming that experimentally from equation [2] one obtains a  $K_{Mg}^{Ca}$  value of 1 for a

given soil, then magnesium is equivalent to calcium and equation [4] can be rearranged to look as follows:

$$\frac{\text{ClayNa}^*}{\text{CEC}-\text{ClayNa}} = K_{\text{Na}}^{\text{Ca,Mg}} \quad [5]$$

where CEC = Clay (Ca + Mg + Na)

Further rearrangement would yield the following two equations.

$$\text{Sodium Adsorption Ratio (SAR)} = \frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2} \frac{(\text{Na}^+)^{1/2}}{\text{Ca}^{2+} + \text{Mg}^{2+}} \quad [6]$$

where  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  concentrations are in mmol(+)/l and

$$\text{Exchangeable Sodium Percentage (ESP)} = \frac{\text{ClayNa}}{\text{CEC}} \quad [7]$$

At a certain SAR a certain portion of the clay cation exchange capacity is dominated by the sodium ion. The United States Soil Salinity Laboratory staff (1954) has shown that at an SAR of 15 there is an ESP of 15, and furthermore, they have shown that at an SAR - ESP of 15 clays will undergo dispersion (causing high sediment loads in water). The same relationship does not hold for shale-clays whose mineralogy is dominated by kaolinite.

In describing the double layer theory, it was pointed out that the thickness of double layer for a certain type of clay was controlled by the ion concentration of the solution. However, the force by which clay particles will attract each other to form floccules is also a function of the ratio of the monovalent cations to the polyvalent, to be precise, the SAR. The latter indirectly gives the percent of exchange sites occupied by the sodium. The SAR modifies the predicted frequency of successful collisions since it is associated with a diffuse double layer.

The most frequently discussed interaction in explaining flocculation in a clay suspension system (sediment pond) is edge to face clay interaction. All clay types have, to a certain degree, edge pH-dependent charge (Balland et



al. 1980) but in the kaolinite systems it is more dominant. When kaolinite exhibits maximum edge positive charge due to low pH, then the negative charge of a clay particle surface is attracted to the positive edge of another particle and flocculation occurs. This point is also referred to as the point of zero point of charge (pHzpc) (Van Raij and Peech, 1972). This type of flocculation can be disrupted in three ways: First, by adding a relatively small amount of salt which in essence will "screen" the opposing charge sites. Second, by adding a different clay mineral to the suspension one will also produce a screening effect (Arora and Coleman, 1971; Quirk and Schofield, 1955). Third, raising the suspension pH will decrease the positive charge, thus the degree of attraction between the clay particles will be considerably reduced (Quirk and Schofield, 1955).

#### Dispersion/Flocculation Experiments

Dispersion/flocculation experiments were carried out to study the effect of pH and SAR on the settling rates of colloidal dispersed solids, and to observe the influence of the interaction, between pH and SAR and ionic strength and SAR on the settling characteristics of the spoil colloidal particles.

The clay-particle settling simulation studies were carried out in 50-ml 20-cm height glass test tubes. To each of the test tubes 2 grams spoil sample was added along with 50-ml of the appropriate solution. The types of solutions used are given in Tables 1 and 2. Adjustments for pH were made with sodium hydroxide. The test-tubes with the spoil sample were rinsed 4 times with 40-ml of the appropriate equilibrating solution. They were shaken and percent transmittance was taken with a Brinkman PC800 Colorimeter at 560 nm, equipped with an immersable probe. Measurements were taken at 5-cm depth with respect to time. The time span between measurements was variable and dependent on the dispersive properties of the sample tested.

The pH and EC of each solution was taken at the end of the transmittance measurements. Cation determination was carried out by atomic absorption spectrophotometry. The relationship between percent transmittance and  $\text{mg L}^{-1}$  suspended solids, along with the code number for each sample is given in Research Report No. 150 (Evangelou et. al. 1984).

The determination of pHzpc was carried out by potentiometric titrations (Van Raij and Peech, 1972).

## CHAPTER III - DATA AND RESULTS

### Solution Composition and Dispersion/Flocculation Experiments

Solution composition of original solutions used to equilibrate the spoil samples is given in Tables 1 and 2. The solution composition after equilibration with the spoil samples has taken place is given in Tables 3,4,5 and 6. Spoil sample chemistry and mineralogy are given in Research Report No. 150 (Evangelou, et. al. 1984).

Figure 1 shows representative titration graphs of the spoil samples. According to theory (Van Raij and Peech, 1972) the crossover point of the different ionic strength plots is the pH of the zero point of charge (pHzpc). The pHzpc can be considered as the point of coflocculation. In other words at this pH, minimum suspended solids would be observed. The graphs in figures 1 and 2 point out that the pHzpc for these spoil samples is too low to be of practical importance in controlling suspended solids in coal mine sedimentation ponds. The data in Fig. 1 and 2 also demonstrate that an increase in pH so that it meets federal standards (pH range 6 -9) would have drastic effects on the concentration of suspended solids.

The data in Figures 3 through 10 (also Tables 1 through 6 in the Appendix) demonstrate the influence pH and SAR have on the settling characteristics of the suspended colloidal particles. As the pH increases the rate of particle settling decreases. Also, as the SAR increases, the rate of particle settling decreases. However, the influence of SAR on particle settling had minimum influence at the lowest pH 5.2).

Table 1. Composition of original solutions with which the spoil samples were brought to equilibrium at pH 5.2 and 7.2.

Solution A				Solution B			
Ca - meq/l -	Na	EC mmhos cm <sup>-1</sup>	SAR (mmol l <sup>-1</sup> ) <sup>1/2</sup>	Ca - meq/l -	Na	EC mmhos cm <sup>-1</sup>	SAR (mmol l <sup>-1</sup> ) <sup>1/2</sup>
3.204	0.004	0.411	0.003	5.848	0.007	0.736	.004
0.814	3.665	0.454	5.746	2.332	6.041	0.848	5.595
0.297	3.866	0.463	10.038	1.087	7.452	0.868	10.110
0.103	4.228	0.464	18.623	0.342	8.947	0.883	21.651
0.024	4.210	0.465	38.257	0.100	8.654	0.890	38.692

Table 2. Composition of Original solutions with which the spoil samples were brought to equilibrium at pH 5.2 and 7.2.

Solution C				Solution D			
Mg --meq/l	Na	EC -mmhos cm	SAR (mmolL <sup>-1</sup> ) <sup>1/2</sup>	Mg -meq/L-	Na	EC mmhos cm <sup>-1</sup>	SAR (mmolL <sup>-1</sup> ) <sup>1/2</sup>
4.073	0.042	0.418	0.012	5.668	0.012	0.708	0.007
0.792	4.452	0.495	7.007	1.615	7.432	0.850	8.270
0.214	4.352	0.466	13.298	0.853	8.302	0.892	12.716
0.040	4.574	0.472	32.117	0.268	9.777	0.907	26.676
0.018	4.431	0.466	46.078	0.066	9.075	0.901	49.886

Table 3. Composition of solutions in equilibrium with the spoil sample at pH 5.2.

Solution A				Solution B			
Ca	Na	EC	SAR	Ca	Na	EC	SAR
meq /l-	mmhos cm <sup>-1</sup>	(mmolL <sup>-1</sup> ) <sup>1/2</sup>	(mmolL <sup>-1</sup> ) <sup>1/2</sup>	meq /l	mmhos cm <sup>-1</sup>	(mmol L) <sup>1/2</sup>	(mmol L) <sup>1/2</sup>
----- Sample 100-----							
2.729	0.060	0.434	0.051	4.756	0.064	0.764	0.042
0.595	2.949	0.469	5.408	1.608	6.220	0.863	6.937
0.345	3.097	0.472	7.456	0.974	6.696	0.896	9.592
0.062	4.264	0.477	24.054	0.298	8.495	0.907	47.921
0.053	4.478	0.475	27.394	0.100	9.143	0.910	55.932
----- Sample 10-----							
3.310	0.064	0.440	0.050	6.850	0.038	0.764	0.020
0.596	3.717	0.484	6.813	1.964	8.030	0.870	8.103
0.393	3.712	0.492	8.377	0.994	8.030	0.870	12.257
0.216	3.769	0.488	11.470	0.411	8.515	0.912	18.785
0.168	3.720	0.490	12.829	0.260	9.260	0.914	25.702

Table 4. Composition of Solutions in equilibrium with the spoil sample at pH 7.2.

Solution A'				Solution B'			
Ca	Na	EC	SAR	Ca	Na	EC	SAR
-meq/L--	mmhos cm <sup>-1</sup>		(mmolL <sup>-1</sup> ) <sup>1/2</sup>	-meq/l-	mmhoscm <sup>-1</sup>		(mmolL <sup>-1</sup> ) <sup>1/2</sup>
----- Sample 100-----							
3.449	0.081	0.430	0.062	6.578	0.074	0.742	0.041
0.904	3.145	0.468	4.678	2.876	5.506	0.852	4.592
0.373	3.757	0.476	8.706	1.346	6.992	0.882	8.520
0.121	4.046	0.488	16.454	0.492	7.780	0.904	15.719
0.066	4.176	0.484	23.122	0.210	7.996	0.908	24.730
----- Sample 10-----							
3.999	0.114	0.540	0.081	7.211	0.179	0.831	0.094
2.106	3.390	0.614	3.304	3.765	5.420	0.991	3.950
1.456	3.787	0.618	4.442	2.370	6.808	1.004	6.254
1.384	4.124	0.640	4.958	1.877	7.748	1.043	7.998
1.310	4.128	0.629	5.101	1.489	8.278	1.070	9.592

Table 5. Composition of solutions in equilibrium with the spoil sample at pH 5.2.

Solution C				Solution D			
Mg -meq/l	Na	EC -1 mmhos cm	SAR -1) <sup>1/2</sup> (mmolL <sup>-1</sup> ) <sup>1/2</sup>	Mg -meq/l	Na	EC -1 mmhoscm	SAR -1) <sup>1/2</sup> (mmolL <sup>-1</sup> ) <sup>1/2</sup>
-----Sample 100-----							
2.922	0.010	0.410	0.008	6.089	0.016	0.736	0.009
0.395	1.894	0.498	4.262	1.561	5.614	0.838	6.354
0.108	1.937	0.469	8.327	0.771	6.194	0.896	9.976
0.050	3.659	0.482	23.288	0.208	8.167	0.912	25.313
0.303	3.843	0.480	31.147	0.066	8.554	0.912	46.857
-----Sample 10-----							
2.456	0.088	0.442	0.080	6.147	0.033	0.761	0.019
0.804	2.896	0.539	4.566	1.420	5.748	0.874	6.823
0.326	3.052	0.516	7.561	0.813	6.038	0.930	9.470
0.152	3.528	0.512	12.822	0.381	7.062	0.955	16.180
0.133	3.750	0.522	14.525	0.172	7.862	0.957	26.683



Table 6 Composition of solutions in equilibrium with the spoil sample at pH 7.2

Solution C'				Solution D'			
Mg -meq/l	Na -----	EC mmhos cm <sup>-1</sup>	SAR (mmolL <sup>-1</sup> ) <sup>1/2</sup>	Mg -----meq/l	Na -----	EC mmhos cm <sup>-1</sup>	SAR (mmolL <sup>-1</sup> ) <sup>1/2</sup>
----- Sample 100 -----							
3.868	0.047	0.438	0.034	7.172	0.068	0.750	0.036
1.108	2.928	0.539	3.932	1.956	5.305	0.876	5.364
0.294	3.128	0.500	8.150	1.058	6.032	0.942	8.296
0.138	3.459	0.526	13.158	0.402	6.678	0.976	14.893
0.064	3.389	0.512	18.886	0.192	6.740	0.978	21.730
----- Sample 10 -----							
2.748	0.049	0.424	0.042	5.073	0.107	0.714	0.067
0.626	3.372	0.501	6.030	1.410	5.680	0.850	6.768
0.087	3.782	0.481	18.164	0.662	7.015	0.905	12.196
0.041	3.975	0.477	27.714	0.136	7.270	0.869	28.050
0.025	3.907	0.477	35.167	0.082	7.736	0.899	38.138

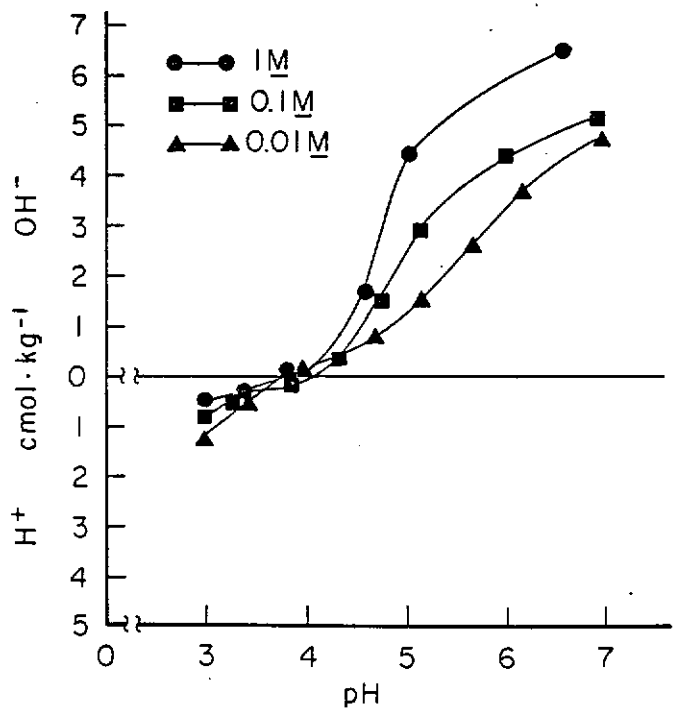


Fig. 1. Potentiometric titrations at various concentrations of NaCl of a randomly selected spoil sample.

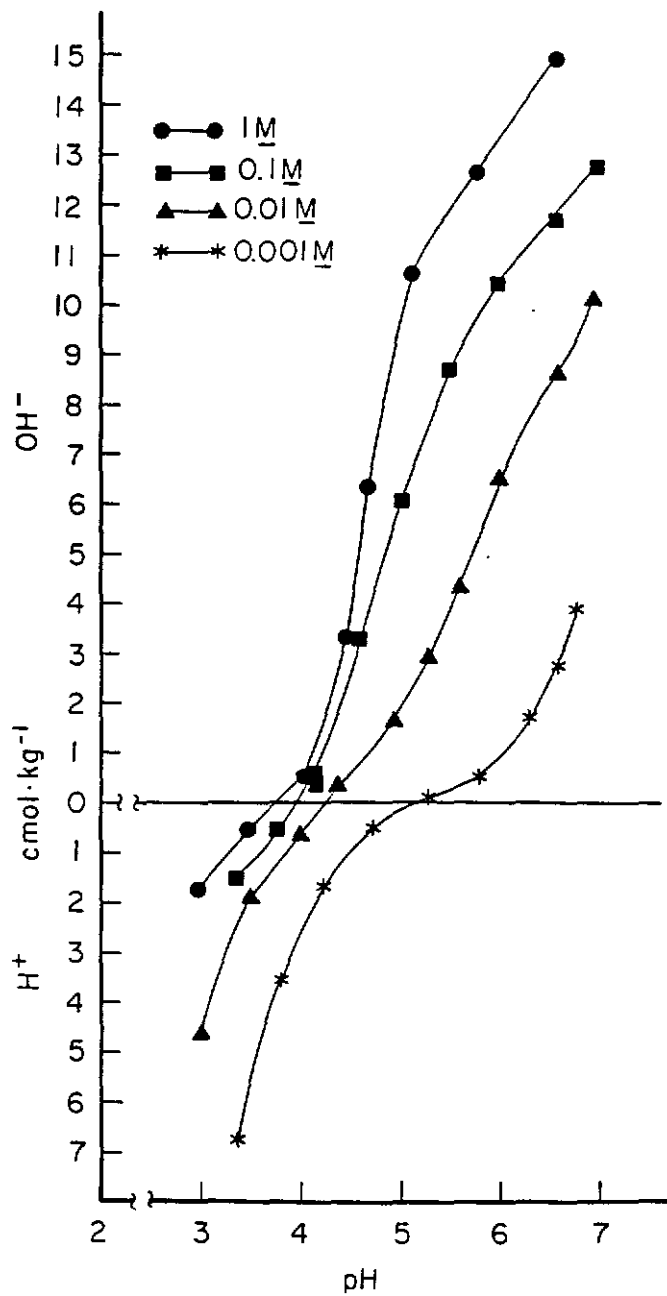


Fig. 2. Potentiometric titrations at various concentrations of NaCl of a randomly selected spoil sample.

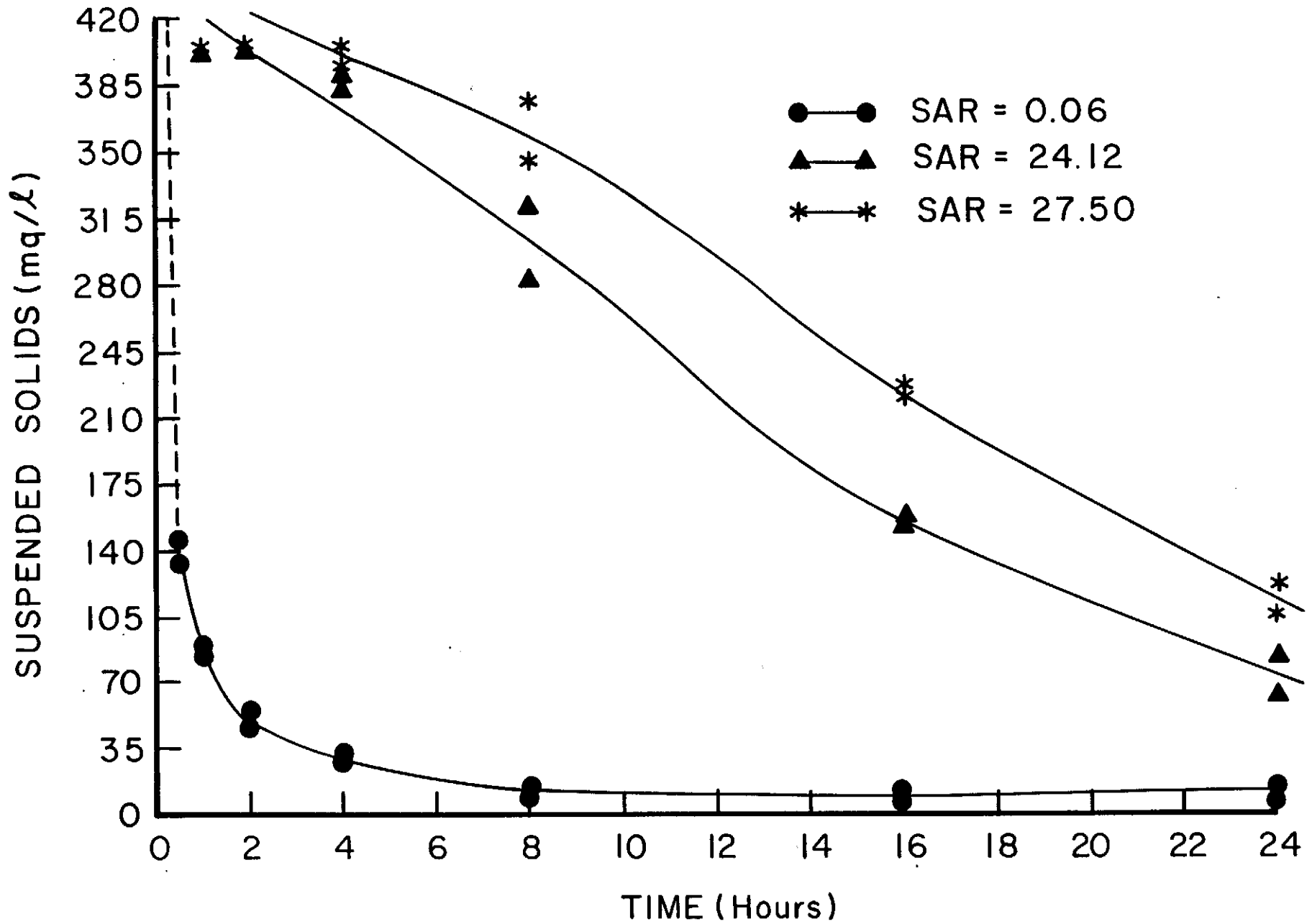


Fig. 3. Kinetics on settling characteristics of sample 100 at various SAR values of Ca-Na system, constant salt concentration of four meq L<sup>-1</sup> and at pH of 5.2.

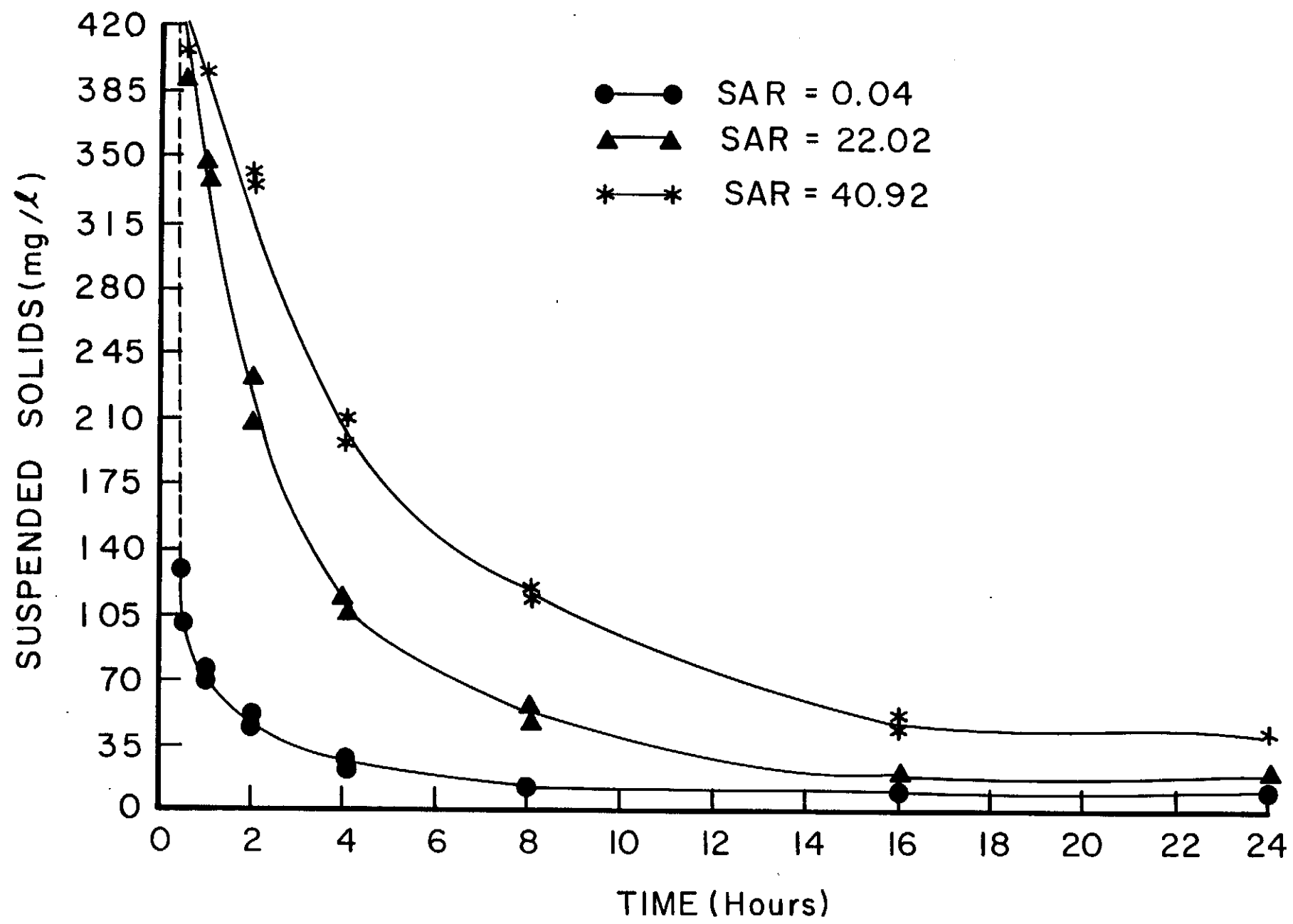


Fig. 4. Kinetics on settling characteristics of sample 100 at various SAR values of Ca-Na system, constant salt concentration of eight meq L<sup>-1</sup> and at pH of 5.2.

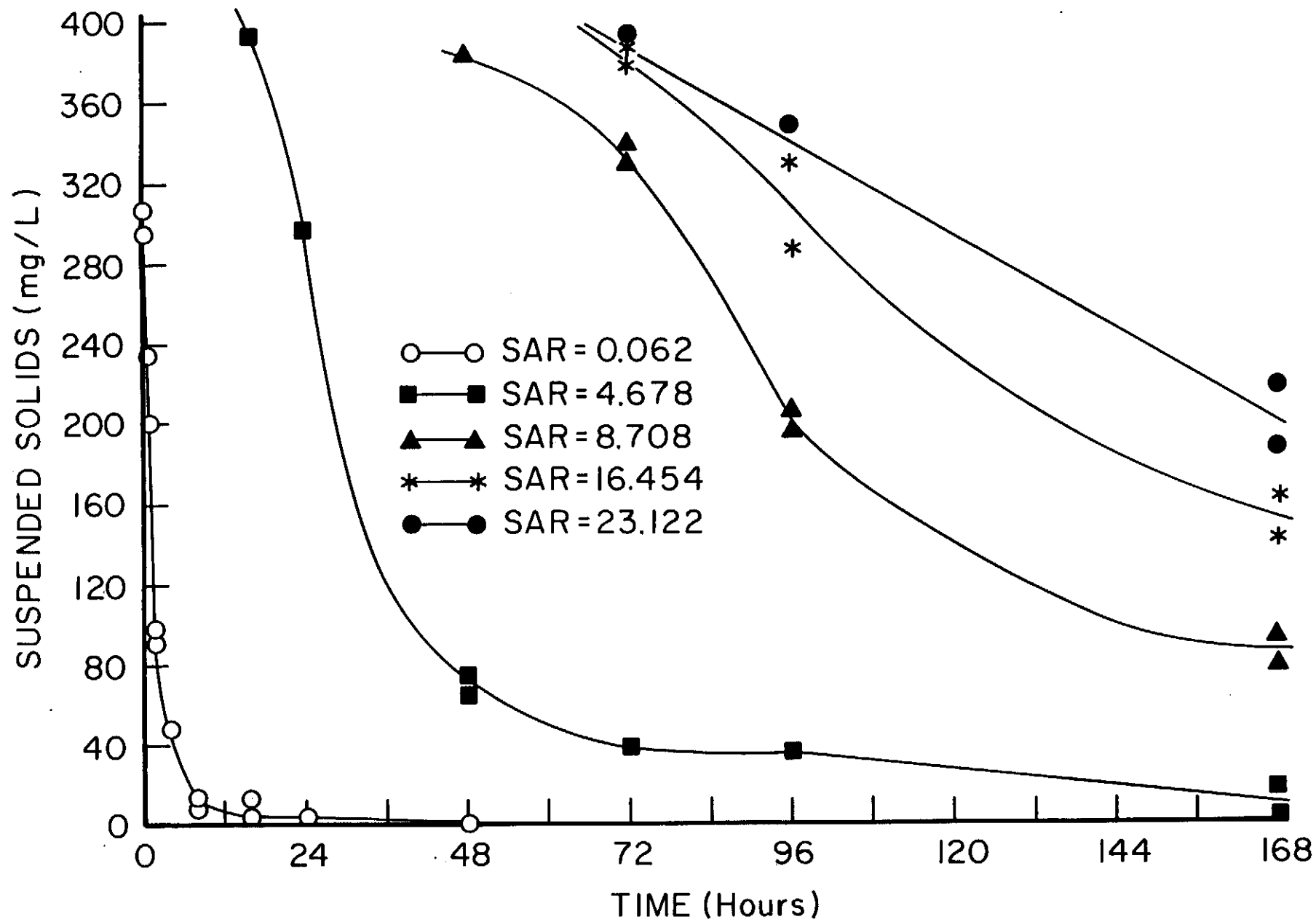


Fig. 5. Kinetics on settling characteristics of sample 100 at various SAR values of Ca-Na system, constant salt concentration of four meq L<sup>-1</sup> and at pH of 7.2.

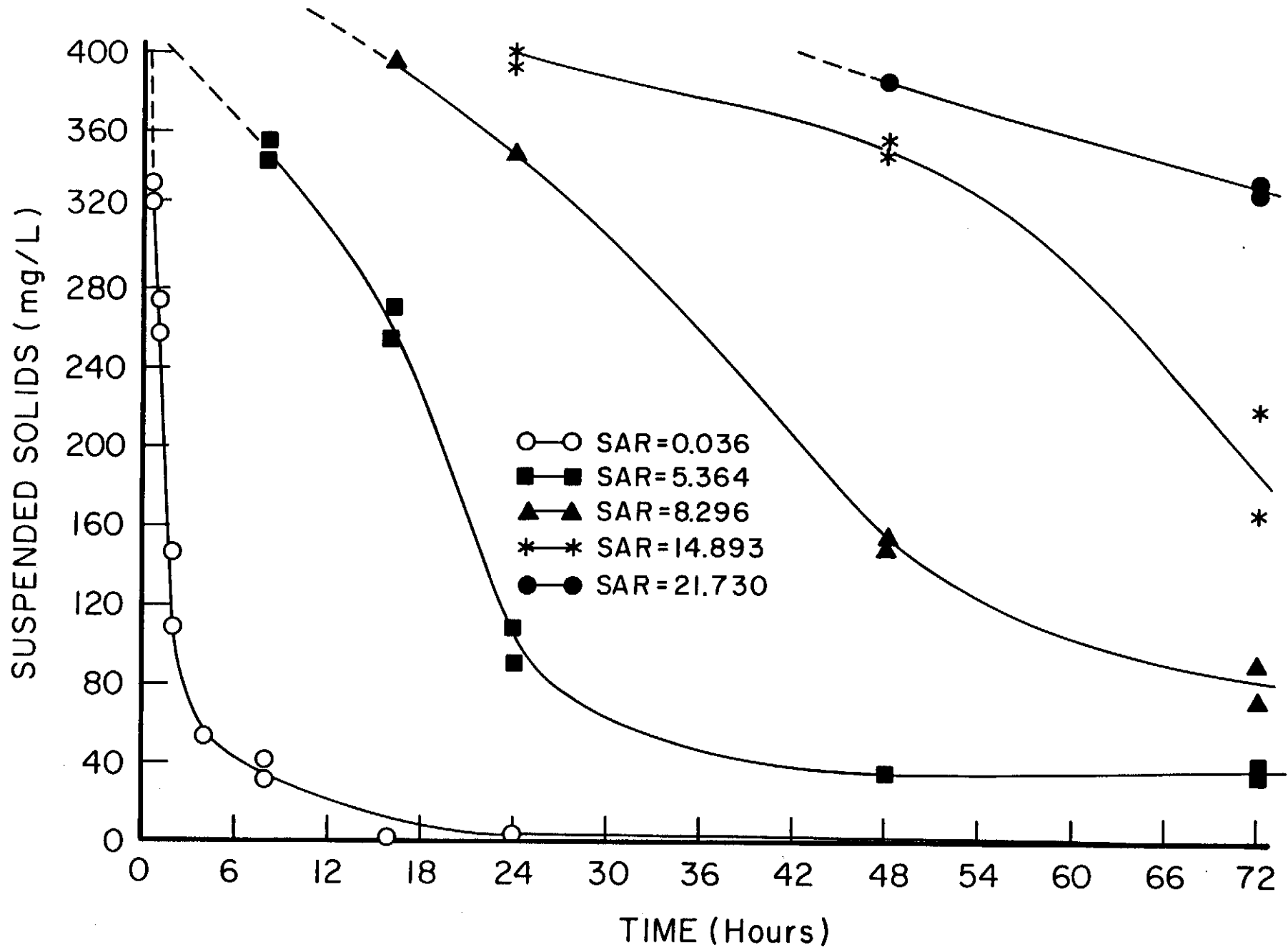


Fig. 6. Kinetics on settling characteristics of sample 100 at various SAR values of Ca-Na system, constant salt concentration of eight meq L<sup>-1</sup> and at pH of 7.2.

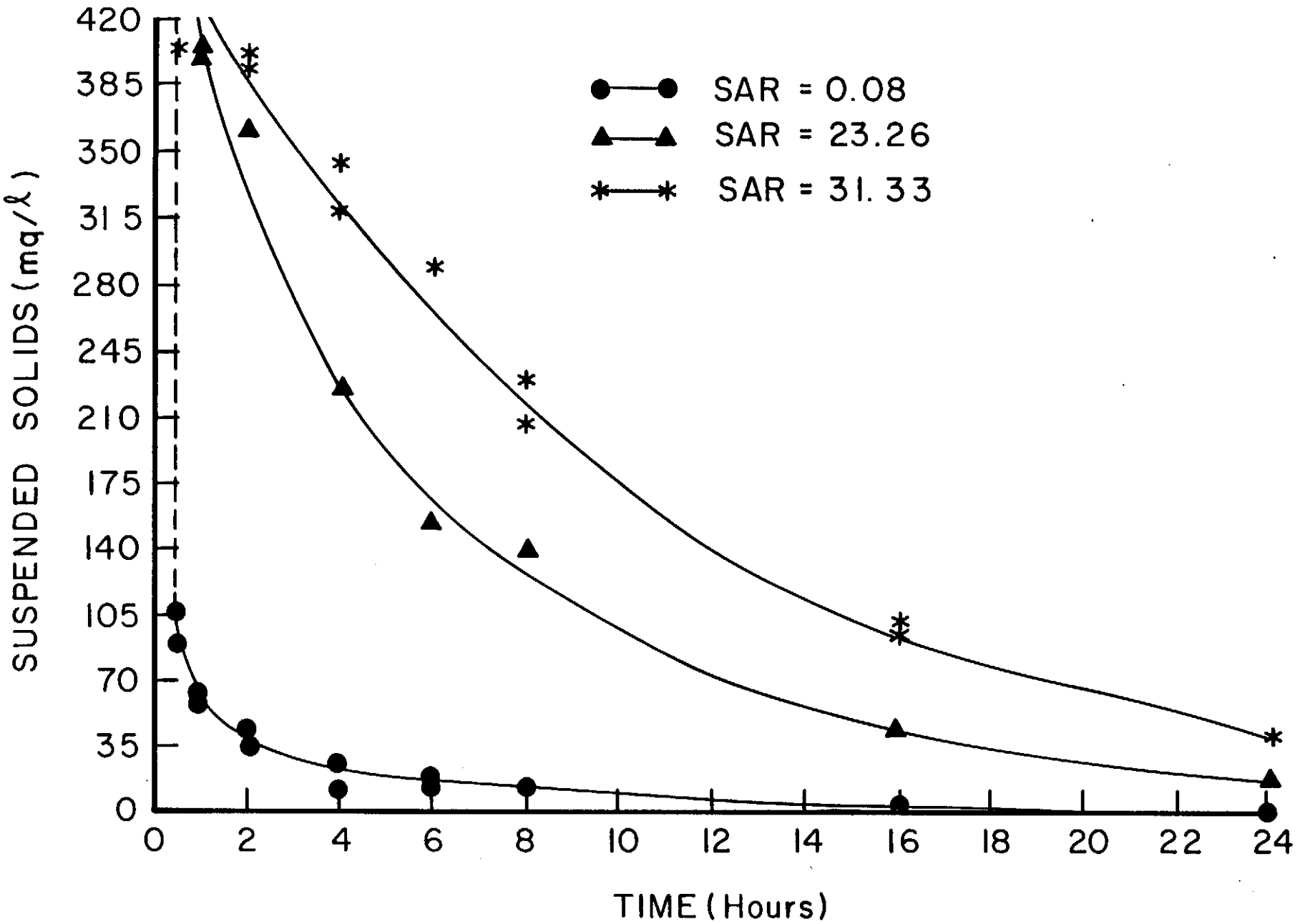


Fig. 7. Kinetics on settling characteristics of sample 100 at various SAR values of Mg-Na system, constant salt concentration of four meq L<sup>-1</sup> ant at pH of 5.2.



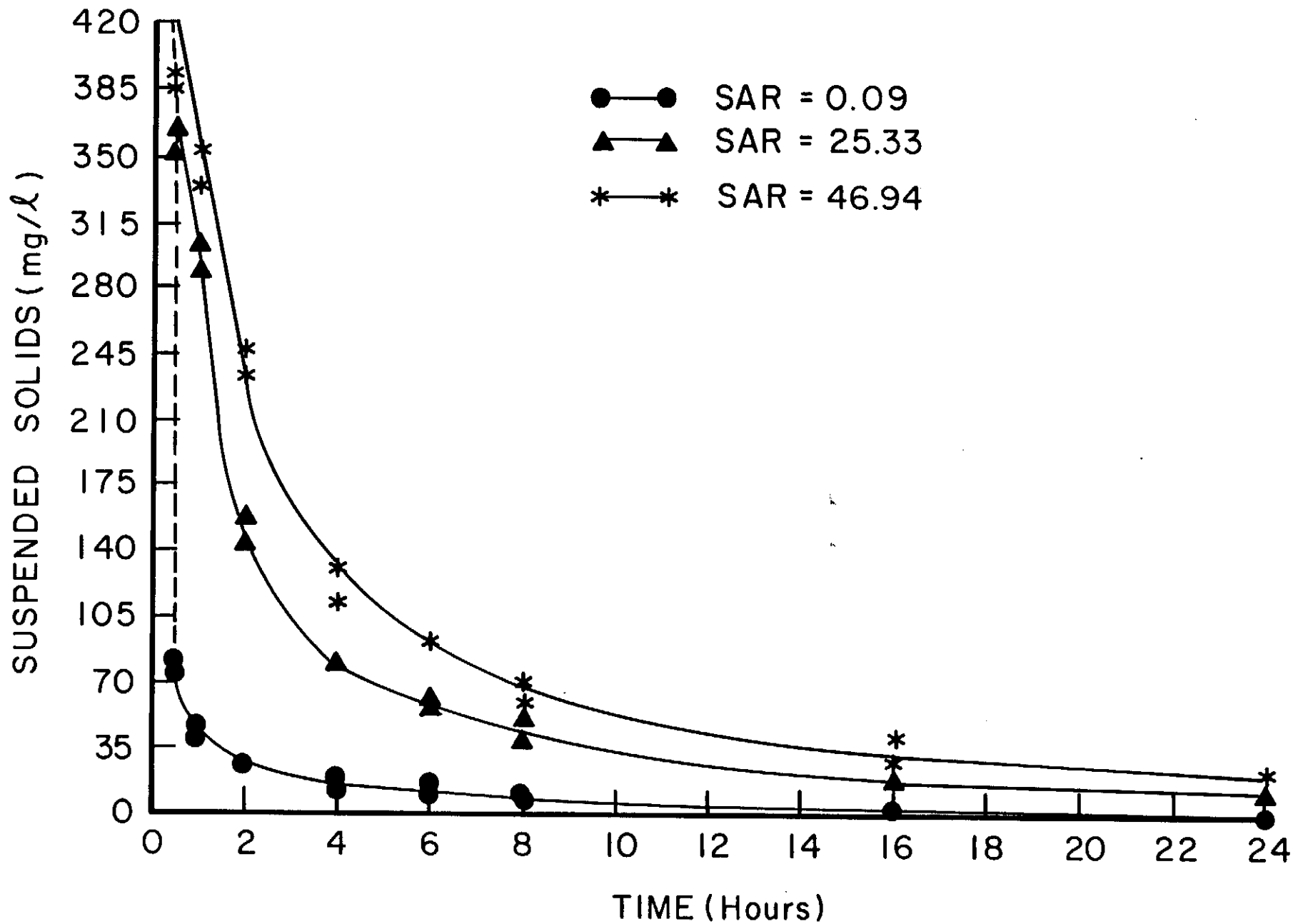


Fig. 8. Kinetics on settling characteristics of sample 100 at various SAR values of Mg-Na system, constant salt concentration of eight meq L<sup>-1</sup> and at pH of 5.2.

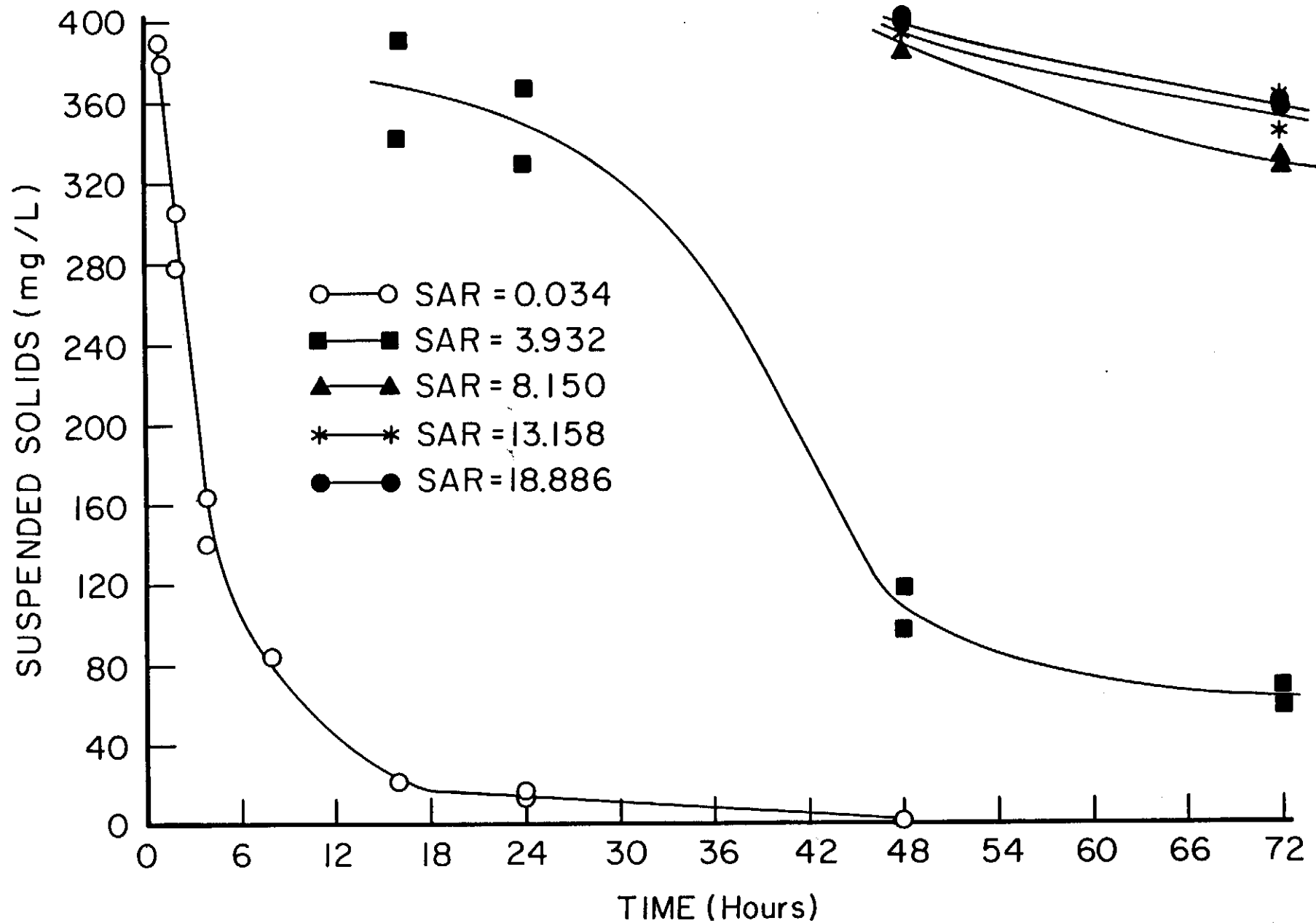


Fig. 9. Kinetics on settling characteristics of sample 100 at various SAR values of Mg-Na system, constant salt concentration of four meq L<sup>-1</sup> and at pH of 7.2.

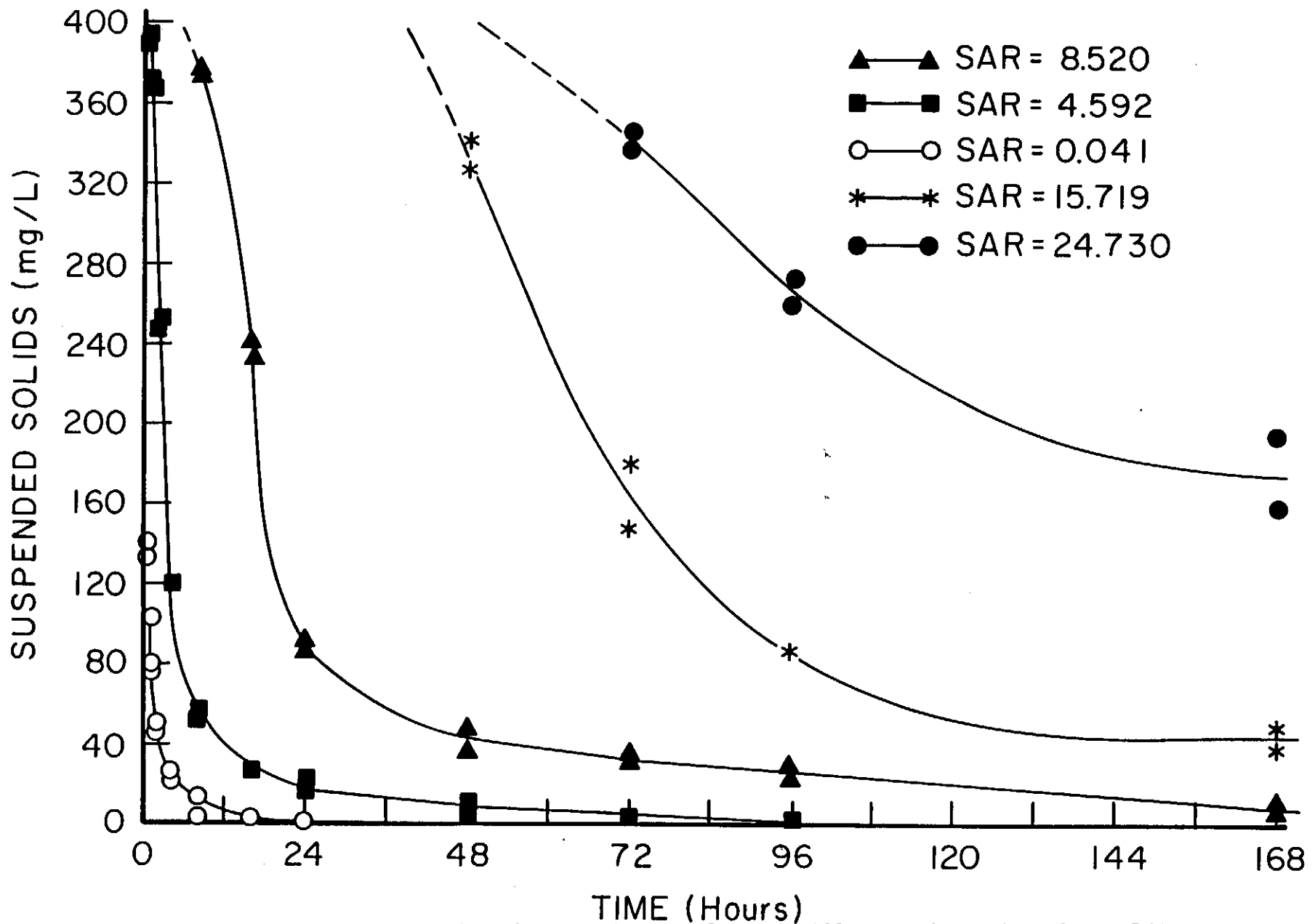


Fig. 10. Kinetics on settling characteristics of sample 100 at various SAR values of Mg-Na system, constant salt concentration of eight meq L<sup>-1</sup> and at pH of 7.2.

The data in figures 3 through 10 also demonstrate that as the ionic strength increases, a concomitant increase in the SAR had a minimum effect on increasing the rate of settling of suspended solids. The substitution of calcium by magnesium had a suppressing effect on the settling rates.

## CHAPTER IV - CONCLUSIONS

This study focused on the behavior of colloidal suspended solids in coalmine sedimentation ponds. In the first phase of this study (Research Report No. 150 Evangelou et. al. 1984) the following points were made:

(1) In order to minimize suspended solids in water released from sedimentation ponds, or for that matter control sediment concentrations in biologically active water reservoirs, the chemistry of the water in conjunction with the chemistry and mineralogy of the suspended solids should be studied.

Upon establishing that indeed double layer interactions are the determining factor in dictating concentration of suspended solids, one may use the RI concept as a means of predicting potential concentrations of suspended solids. In fact, after establishing a calibration curve of RI vs concentration of suspended solids by the use of a field spectrophotometer, the test could easily be run on site.

Another important contribution of this study is in managing suspended solids in coal mine sedimentation ponds. Assuming one establishes that an existing or future sedimentation pond responds to double layer interactions, then one may control suspended solids by manipulating water chemistry. This manipulation can be carried out several ways. One is by introducing a calcium source in the streams leading to the pond. This source could most likely be gypsum. This form of calcium, because of its relatively slow rate of dissolution in water when in the size of gravel, could be a long term solution. Another way is to divert streams of known water concentration and composition into a pond of high suspended solids that would cause clay flocculation. Finally, the design of the pond could be such that a high

spoil-water ratio is introduced into the pond upon a rainfall event, thus maintaining an RI value conducive to clay flocculation.

Understanding the forces that govern suspended solids and managing them accordingly is an important long term goal. More often than not, the addition of constituents in the water such as commercially available flocculants would not be required. In fact, long term use of such substances in low management natural systems such as sedimentation ponds, may backfire, leading to adverse affects on water chemistry and surprisingly enough, even an increase in suspended solids.

In the second phase of this study the following points have been established: (1) Because of the low charge clay mineral dominance in coal spoils of Kentucky, the pH range of coflocculation of the colloidal particles is below that allowed by federal standards (below pH 6). (2) Upon increasing the pH by the addition of limestone, suspended solids drastically increase and their rate of settling decreases. (3) The rate of settling of clay colloidal particles appears do be controlled also by the SAR which is altered in sedimentation ponds by the use of sodium hydroxide (NaOH). (4) The ability of the higher SAR to decrease rates of settling of suspended solids can be modified by decreasing pH and/or increasing total solids dissolve. (5) Magnesium appears to have a possitive effect on increasing the rates of settling for some samples but negative for others.

The second phase of the study points out that pH, total dissolved solids and composition (SAR) have a direct effect on rate of suspended solid settling. In order to minimize suspended solids, pH should be kept upon increasing the pH to a minimum; total dissolved solids should be increased but SAR should be maintained much below 10. The latter can be controlled by using

limestone as a neutralizer. When NaOH is to be used, the addition of Ca in the form of gypsum should be considered.

Finally, contrary to what is believed by mining personnel and government environmental law enforcement agencies, suspended solids cannot be classified into those that are settleable and those that are not. If the water chemistry of the pond is changed, so called settleable solids can become nonsettleable and vice-versa.

## NOMENCLATURE

EC	Electrical conductance ( $\text{mmhos}/\text{cm}^{-1}$ or $\text{mhos}/\text{cm}^{-1}$ )
	Surface potential (mvolts)
x	Distance from surface (cm)
$K_{\text{Mg}}^{\text{Ca}}$	Selectivity coefficient for Ca-Mg exchange
$K_{\text{Na}}^{\text{Ca}}$	Selectivity coefficient for Ca-Na exchange
$K_{\text{CaMg}}^{\text{K}}$	Selectivity coefficient for K-(Ca+Mg) exchange
$K_{\text{CaMg}}^{\text{Na}}$	Selectivity coefficient for Na-(Ca+Mg) exchange
SAR	Sodium adsorption ratio
ESP	Exchangeable sodium percentage
e	charge of electron ( $1.6 \times 10^{-19}$ coulombs)
	dielectric constant ( $89 \times 10^{-12}$ coulombs $\text{V}^{-1} \text{cm}^{-1}$ )
kT	Boltzmann constant times absolute temperature ( $0.41 \times 10^{-20}$ V coulombs at 20 degrees C).
N	Avogadro's number ( $6.03 \times 10^{23}$ mole <sup>-1</sup> )
I	Ionic Strength (moles $\text{L}^{-1}$ ).
RI	Repulsive index (unitless).
EX	Exchangeable cations ( $\text{meq}(100\text{g})^{-1}$ )



APPENDIX

Table 1. Suspension behavior of spoil sample 10 at pH 5.2 for Ca - Na system.

SAR <sub>1</sub> (mmol L <sup>-1</sup> ) <sup>1/2</sup>	EC mmhos cm <sup>-1</sup>	% Transmittance							
		0	Time (Hours)						
		25	0.50	1	2	3	4	6	8
----- -4 meq/l -----									
0.050	0.440	48.2	64.4	72.2	78.8	82.8	87.6	93.4	94.1
6.813	0.484	44.8	55.8	61.3	70.4	77.1	79.0	91.2	92.4
8.377	0.492	45.0	52.2	59.0	66.8	72.1	75.6	89.0	92.4
11.470	0.488	40.4	50.4	52.5	56.5	68.4	70.0	90.4	90.8
12.829	0.490	27.2	41.8	46.2	57.2	66.0	69.8	87.6	91.1
----- -8 meq/l -----									
0.020	0.764	31.0	55.2	72.6	75.0	81.4	86.4	90.9	90.8
8.103	0.870	35.2	51.2	65.4	71.3	78.5	84.3	90.4	90.4
12.257	0.899	34.0	56.0	67.3	73.2	76.3	80.9	88.6	88.6
18.785	0.912	38.3	52.8	64.7	71.2	74.6	78.6	89.6	89.6
25.702	0.914	40.9	52.4	60.8	63.6	73.5	80.0	76.0	88.8

Table 2. Suspension behavior of spoil sample 10 at pH 5.2 for Mg - Na system.

SAR <sub>i</sub> (mmol <sup>-1</sup> ) <sup>1/2</sup>	EC mmhos cm	% Transmittance					
		Time (Hours)					
		0.5	1	2	4	6	8
----- 4 meq / l -----							
0.079	0.042	58.0	73.2	89.6	90.8	90.3	90.4
4.583	0.539	47.7	63.4	75.6	88.4	88.9	89.1
7.570	0.516	47.4	50.0	69.8	86.8	86.5	88.0
12.826	0.512	35.6	45.4	60.0	81.6	83.4	84.6
14.602	0.522	34.2	41.5	55.1	79.5	82.6	83.2
----- 8 meq / l -----							
0.019	0.761	69.8	78.4	86.6	89.2	90.5	91.9
6.820	0.874	66.2	75.9	79.9	87.0	88.2	91.3
9.472	0.930	61.8	70.6	75.0	85.5	87.4	89.1
16.162	0.944	52.6	63.4	69.2	79.2	84.2	88.2
26.670	0.958	52.6	60.2	67.2	78.6	84.0	88.6

Table 3 Suspension behavior of spoil sample 10 at pH for Mg - Na System

SAR (mmolL <sup>-1</sup> ) <sup>1/2</sup>	EC mmhos cm <sup>-1</sup>	% Transmittance									
		Time (Hours)									
		0.5	1	2	4	16	24	48	72	96	120
----- -4 meq/l-----											
0.042	0.424	16.3	27.3	44.8	67.0	91.4	94.4	97.4	98.5	98.0	99.3
6.030	0.501	--	---	---	---	13.0	39.3	59.2	75.4	81.0	81.7
18.164	0.481	--	---	---	---	---	---	13.3	32.0	53.8	64.2
27.714	0.477	--	---	---	---	---	---	---	---	---	1.9
35.167	0.477	--	---	---	---	---	---	---	---	---	1.6
----- 8 meq/l-----											
0.067	0.714	54.8	61.4	76.0	88.2	96.3	97.8	98.8	99.2	99.5	99.7
6.768	0.850	2.4	4.8	15.5	40.3	87.5	91.5	94.1	95.9	97.1	97.6
12.196	0.905	--	--	1.2	5.8	48.3	70.3	80.5	83.6	86.2	85.9
28.050	0.869	--	--	--	3.4	32.7	52.0	73.6	84.4	86.1	88.4
38.138	0.899	--	--	--	--	--	--	1.2	3.2	14.2	35.5

Table 4 Suspension behavior of spoil sample 10 at pH 7.2 for Ca-Na system.

SAR (mmol L <sup>-1</sup> ) <sup>1/2</sup>	EC <sub>1</sub> mmhos cm <sup>-1</sup>	% Transmittance										
		Time (Hours)										
		0.25	0.50	1	2	3	4	6	8	16	24	
----- -4 meq / l-----												
0.081	0.540	9.8	22.7	40.5	60.6	74.0	79.2	80.7	90.9	94.7	97.6	
3.304	0.614	-	2.4	9.6	28.2	49.2	62.2	68.8	82.0	91.2	94.7	
4.442	0.618	-	-	1.4	6.6	17.4	31.2	44.2	70.8	87.0	88.3	
4.958	0.640	-	-	1.7	5.6	15.0	28.5	40.7	69.0	86.7	86.8	
5.101	0.629	-	-	1.4	4.4	11.4	20.4	31.6	62.8	78.8	82.6	
----- -8 meq / l-----												
0.094	0.831	16.9	34.9	58.0	79.2	81.6	86.6	90.4	92.4	95.7	98.2	
3.950	0.991	3.0	8.1	23.0	51.4	63.0	71.6	82.8	88.5	93.8	97.0	
6.254	1.004	-	2.4	8.1	31.0	46.1	61.0	73.5	80.3	90.4	94.9	
7.998	1.043	-	1.0	2.6	13.8	25.8	37.4	56.4	80.5	88.5	91.4	
9.592	1.070	-	-	1.2	6.1	13.5	20.4	35.6	71.2	80.6	85.2	

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