Wat. Res. Vol. 26, No. 6, pp. 817–823, 1992
Printed in Great Britain. All rights reserved

0043-1354/92 $5.00 + 0.00

SEAWATER FLOCCULATION OF EMULSIFIED OIL AND ALKALINE WASTEWATERS

G. M. Ayoub[1], S.-I. Lee[2], C. N. Mazidji[3], I.-S. Seo[2], H.-M. Cho[2] and B. Koopman[4]*Ⓜ
[1]Faculty of Engineering and Architecture, American University of Beirut, Beirut, Lebanon,
[2]Department of Environmental Engineering, Chungbuk National University, Cheongju, 360-763, Korea,
[3]Sirrine Environmental Consultants, Greenville, SC 29616 and
[4]Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL 32611-2013, U.S.A.

(First received January 1991; accepted in revised form November 1991)

Abstract—Seawater flocculation at high pH was investigated for the removal of emulsified oil and suspended solids from wastewater. As little as 2% seawater by volume, in conjunction with lime or caustic for pH adjustment, was required to achieve good flocculation of the oil–water emulsion. The same amount of seawater allowed efficient removal of suspended solids from alkaline industrial wastewaters and oxidation pond effluent having pH of 10.6 and higher, without addition of an OH^- source. Effective flocculation was associated with the precipitation of 2–3.5 g equiv m^{-3} of Mg^{2+}. The minimum seawater concentration for effective flocculation, in relation to pH, was predicted successfully based on the solubility of magnesium in wastewater–seawater mixtures.

Key words—emulsified oil, flocculation, industrial wastewater, lime, magnesium, seawater

INTRODUCTION

Flocculation of wastewater at high pH achieves highly efficient removal of particulates, colloids and certain dissolved materials such as humic acids and heavy metals. Alkaline flocculation has been found to be most effective in suspensions containing relatively high levels of Mg^{2+} ions (Thompson *et al.*, 1972; Folkman and Wachs, 1973; Friedman *et al.*, 1977; Leentvaar and Rebhun, 1982). This is due in part to the positive charge carried by magnesium hydroxide floc (Black and Christman, 1961; Larson and Buswell, 1940), which promotes interaction with negatively charged contaminant particles. Seawater can serve as an economical source of magnesium ions, whereas lime or caustic soda are commonly used as sources of hydroxyl ions. Seawater flocculation with either lime or caustic has been applied successfully for the removal of suspended solids, phosphates and algae from wastewater effluents (Vråle, 1978; Ferguson and Vråle, 1984; Ayoub and Koopman, 1986; Ayoub *et al.*, 1986).

The objectives of the present research were to explore additional applications of seawater flocculation and to gain a better understanding of the conditions under which effective flocculation is achieved. Emulsified oil was one of the pollutants of interest. Oil droplets in water carry negative charges at all pH, regardless of their source (API, 1969; Franzen *et al.*, 1972; Luthy *et al.*, 1978; Nalco Chemical Co., 1979). They should thus interact readily with the positively charged magnesium hydroxide floc. Seawater flocculation could serve as an alternative to the inorganic flocculants (Fe^{2+}, Fe^{3+}, Al^{3+}, lime) now commonly in use to break oil emulsions (Huang and Hardie, 1971; Franzen *et al.*, 1972; Humenick and Davis, 1978; Little and Patterson, 1978; Sadlen *et al.*, 1978; Steiner *et al.*, 1978). Also of interest were industrial wastewaters which are highly alkaline, such as some food processing and textile wastewaters, as well as effluent from oxidation ponds where photosynthesis elevates the pH. Because of their alkaline nature, flocculation of these wastewaters might be achieved merely by addition of seawater, without the need for a supplemental source of OH^- ions. This would represent great cost savings to industries and oxidation pond systems in coastal regions.

MATERIALS AND METHODS

Oil removal experiments

Experiments on oil removal were carried out at the University of Florida. The oily wastewater was prepared in bulk by mixing a measured amount of oil-based, metal-working fluid with tap water. The metal-working fluid was supplied by Cincinnati Milarcon (Cincinnati, Ohio) under the trade name of Cimperial 1011. It was composed of more than 50% mineral oil supplemented with anionic and non-ionic emulsifiers, preservatives and water. Its reported characteristics were: solubility in water (appreciable, emulsifiable) greater than 10%; specific gravity, 1.006; flash point, 188°C; freezing point, −35°C; pH (5.0% metal-working fluid in water), 8.7. Laboratory tests of surface tension and dynamic viscosity were conducted according to ASTM Standards (ASTM, 1986), method A (D 1331-56)

---

*Author to whom all correspondence should be addressed.

and method A (D 2196-81), respectively. Dynamic viscosity was measured with a Brookfield Viscometer operated at a rotational speed of 1.5 rpm and a shear ratio of $5.75\ s^{-1}$. The surface tension of the fluid was found to be $3.56 \times 10^{-2}\ N\ m^{-1}$. Its dynamic viscosity was $0.27\ N\ s\ m^{-2}$. The tap water was lime-softened groundwater having the following typical characteristics: total hardness, $127\ g\ m^{-3}$ as $CaCO_3$; total alkalinity, $48\ g\ m^{-3}$ as $CaCO_3$; Ca^{2+}, $63\ g\ m^{-3}$ as $CaCO_3$; Mg^{2+}, $64\ g\ m^{-3}$ as $CaCO_3$; Cl^-, $30\ g\ m^{-3}$; HCO_3^-, $42\ g\ m^{-3}$ as $CaCO_3$; CO_3^{2-}, $6\ g\ m^{-3}$ as $CaCO_3$; pH, 8.2–8.4; TDS, $183\ g\ m^{-3}$. Seawater used in the experiments was collected off the eastern Florida coast at Crescent Beach. The salinity value, based on a measured specific gravity of 1.0265 at 21.5°C, was 37.6 parts per thousand (APHA *et al.*, 1985). Corresponding Na^+, Ca^{2+} and Mg^{2+} concentrations were 11560, 444 and $1390\ g\ m^{-3}$, respectively (McAllister and Corcoran, 1969).

A jar test apparatus having stainless steel paddles and stirrer was used for the flocculation tests. Paddles had a height of 2.5 cm and diameter of 7.6 cm. The jars were made of acrylic plastic and had dimensions of 11.5 × 11.5 × 25 cm. Values of mean velocity gradient (G) were determined from rotational speeds using the correlation of Cornwell and Bishop (1983).

Five trials with lime were carried out. Six jars of the test water were used in each trial. Freshly mixed 5% lime slurry was added to the oil/tap water emulsion in a 20 l. glass carboy. The mixture was then transferred to the individual jars. Next, seawater was added in predetermined volumes. The final liquid volume in each jar was 2.0 l. Flash mixing at a G of $135\ s^{-1}$ was initiated immediately following addition of seawater and was continued for 1 min. The mixing speed was then reduced to impart a G of $23\ s^{-1}$ and held at this level for 30 min. At the end of a 45 min quiescent settling period, 800 ml of each supernatant was carefully transferred to a 1.0 l. extraction funnel for measurement of oil concentration. An additional 400 ml of supernatant was decanted for determination of pH, calcium hardness, total hardness, phenolphthalein alkalinity and total alkalinity. The same general procedure was applied when caustic soda was used to elevate the pH of the oil–water emulsion. Four trials, each with six jars, were performed.

In order to facilitate comparisons, quantities of lime, caustic soda, calcium, magnesium and alkalinity are expressed in terms of gram equivalents. Lime and caustic soda dosages are relative to the test water volume before seawater addition. Seawater concentrations are expressed on a volumetric basis relative to the final volume of each mixture.

The target extractable oil concentration in the test water before seawater addition was $1000\ g\ m^{-3}$. Oil concentrations were determined by the extraction technique of *Standard Methods* (APHA *et al.*, 1985), method 503A. Salinity was adjusted to the equivalent of 20% (v/v) seawater before extracting the oil in order to compensate for the variation in dissolved solids content of the water which otherwise could cause inconsistent variations in extraction efficiency. Alkalinity, pH, total hardness, calcium hardness and salinity were determined according to *Standard Methods* (APHA *et al.*, 1985) using methods 403, 423, 314B, 311C, 210B, respectively. All experiments were conducted at room temperature (22 ± 1.0°C).

Pollutant removals were computed according to the following formula:

$$\text{removal (\%)} = 100 - \frac{C_s}{C_0}\left[\frac{100}{100 - S}\right] \qquad (1)$$

where

C_0 = pollutant concentration in wastewater, before seawater addition and flocculation
S = volumetric seawater concentration (%)
C_s = pollutant concentration after seawater addition and flocculation.

The term in [ ] adjusts for the dilution of C_0 by seawater.

Alkaline wastewater experiments

Experiments on seawater flocculation of alkaline wastewater were carried out at Chungbuk National University. The alkaline wastewaters were obtained from a cotton towel manufacturing plant, vegetable milk extraction facility and a pilot scale oxidation pond. Their characteristics are given in Table 1. Seawater was obtained on the southern coast of Korea near Haeundae Beach. Its salinity was 35 parts per thousand. Corresponding Ca^{2+} and Mg^{2+} concentrations were 411 and $1293\ g\ m^{-3}$, respectively (McAllister and Corcoran, 1969).

A jar test apparatus similar to that described previously was used in the experiments. In the first of four sets of experiments, wastewater from the two industrial sources and oxidation pond effluent was combined with seawater in various proportions under rapid mixing conditions ($G = 250\ s^{-1}$). The final liquid volume in each jar was 2.0 l. After 1 min of rapid mixing, the rotational speed was reduced to give a G value of $22\ s^{-1}$. This was held for 20 min. Finally, a quiescent settling period of 30 min was allowed. At the end of the settling period, 250 ml of supernatant was decanted from each jar and used for water quality analysis.

The effect of initial pH (pH_i) on seawater flocculation was assessed in the second and third sets of experiments. In set 2, strongly alkaline food processing wastewater (pH = 12.7) was mixed with oxidation pond effluent having a lower pH (9.4) due to inactive photosynthesis. The pH_is of the mixtures ranged from 10.0 to 12.0. The mixtures were flocculated with seawater according to the procedure described. In set 3, strongly alkaline food processing wastewater (pH = 12.6) was blended in varying proportions with weakly alkaline wastewater (pH 9.8) from the same source, giving aliquots with pH_is ranging from 9.8 to 12.6. These were flocculated with seawater as before.

The fourth set of experiments was conducted to determine the roles of calcium and magnesium precipitation in suspended solids removal. NaOH was added to adjust the pH of a stationary phase algal culture (pH 9.5) to values ranging between 9.5 and 12. Seawater was added to give a volumetric concentration of 10% and the aliquots were flocculated as before.

The water quality parameters alkalinity, pH, total suspended solids, total phosphorus, total Kjeldahl nitrogen, chemical oxygen demand and salinity were determined according to *Standard Methods* (APHA *et al.*, 1985), using methods 403, 423, 209D, 424F, 420B, 508A and 210A, respectively. Filterable COD in effluent was measured

Table 1. Characteristics of alkaline wastewaters (units are $g\ m^{-3}$ except for pH and color)

Wastewater type	Total COD	Filtered COD*	TSS	TKN	Alkalinity (as $CaCO_3$)	pH	Color
Textile mill	610	360	350	140	1233	10.6	Blue
Food processing†	850	480	290	65	1333	12.6	Yellow
Oxidation pond	—	—	455	—	166	10.9	Green

*Pore size of 1.2 μm.
†From glass bottle cleaning operation.

on filtrate from Whatman GF/C filters (effective pore diameter = 1.2 μm). Mg and Ca were measured in filtered (through membrane filters with 0.45 μm effective pore diameter) samples by atomic absorption spectrometry (APHA *et al.*, 1985; method 303A). All experiments were conducted at room temperature (25 ± 2°C).

RESULTS AND DISCUSSION

Effect of seawater concentration, chemical dosage and initial pH

The effect of volumetric seawater concentration on oil removal efficiency is shown in Fig. 1. Except for limited removal (approx. 15%) at 20% seawater, the removal efficiencies were insignificant at lime dosages of up to 5.4 g equiv m^{-3} (Fig. 1, top). The removal of oil at low lime dosage and high seawater concentration is attributed to the demulsifying effect of seawater. This was evidenced by free oil that floated to the liquid surface and coated the stirrers and inside of the jar. This phenomenon was not observed in jars with low seawater concentrations. At lime dosages of 10.8 and 16.2 g equiv m^{-3}, about 79% of the oil was removed at a seawater concentration of 2%. The removal efficiency at seawater concentrations of 5% and greater was in the range of 94–97%. The tests characterized by efficient oil removal had extensive floc formation during the flash mix and flocculation phases of the trials. The flocs settled rapidly when mixing was stopped.

Similar results were obtained with caustic soda (Fig. 1, bottom). Almost no removal occurred at caustic dosages of 1.2 and 2.2 g equiv m^{-3} with seawater concentrations of up to 15%. Limited removal was noted at 20% seawater. This was associated with the demulsification and appearance of free oil. Oil removals at caustic dosages of 5.1 and 17.7 g equiv m^{-3} with 5% seawater or greater were excellent. Moderate removal was observed at 2% seawater and a caustic dosage of 17.7 g equiv m^{-3}. This was associated with the formation of small flocs that settled slowly. Excellent removal was obtained at 2% seawater and a caustic dosage of 5.1 g equiv m^{-3}.

The effects of seawater concentration on removals of total suspended solids (TSS) from alkaline wastewaters are shown in Fig. 2. Tests of the three types of wastewater as discharged showed that poor flocculation (0–36% TSS removal) was achieved in the absence of seawater, whereas good flocculation resulted from addition of 10% seawater (Fig. 2, top). Results were variable at intermediate seawater concentrations, whereas flocculation was not improved by addition of more than 10% seawater.

Blending of high pH food processing wastewater with lower pH effluent from the oxidation pond allowed a gradation of initial pH to be obtained. The effect of pH_i on seawater flocculation of these mixtures is shown in the middle of Fig. 2. The minimum

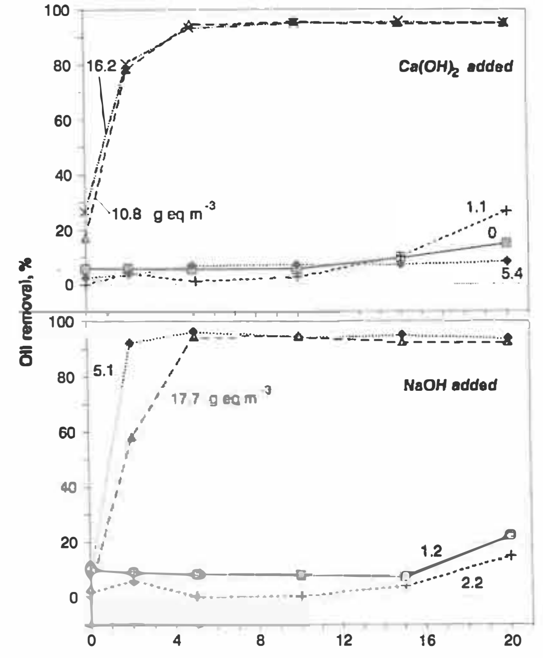

Fig. 1. Effect of seawater concentration and dosage of lime or caustic soda on oil separation efficiency. Top, lime added; bottom, caustic soda added.

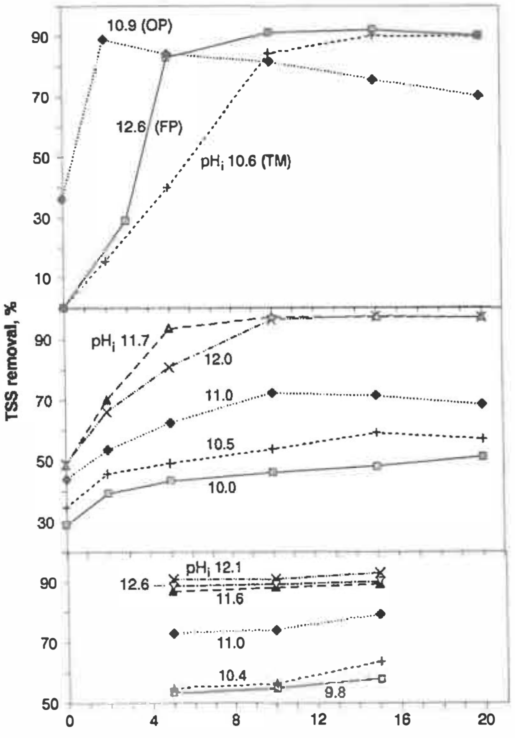

Fig. 2. Effect of seawater concentration and initial pH on suspended solids removal from alkaline wastewaters. Top, food processing wastewater (FP), textile mill wastewater (TM), oxidation pond effluent (OP); middle, mixtures of food processing wastewater and oxidation pond effluent; bottom, mixtures of high pH food processing wastewater with low pH wastewater from the same source.

effective pH_i was somewhat in excess of 11.0, whereas the minimum effective seawater concentration was 5%. Flocculation was not markedly improved at seawater concentrations in excess of 10%. Similar results were obtained with mixtures of high pH and low pH food processing wastewater, as shown at the bottom of Fig. 2.

Removal of nutrients, COD and color

Several water quality parameters in addition to TSS were measured in the experiments with alkaline wastewaters. Removal of these constituents from food processing and textile wastewaters is correlated with TSS removal in Fig. 3. TKN and TSS removal from textile wastewater was almost identical. Good correlation was also exhibited with color removal from textile wastewater and COD removal from food processing wastewater. It is interesting to note that COD removal reached 70%, despite the fact that over half the COD was filterable through 1.2 μm pore size paper. The top of Fig. 4 shows that removal of total phosphorus, TKN, COD and filterable COD was well correlated with TSS removal from oxidation pond effluent. These correlations are specific to the types of wastewater tested, but nonetheless demonstrate the wide range of pollutants removed by seawater flocculation.

Roles of magnesium and calcium in seawater flocculation

At the bottom of Fig. 4 are plotted the filterable magnesium and calcium concentrations after flocculation in the experiments with oxidation pond effluent. The metal concentrations were measured by atomic absorption spectrometry and therefore include both ionic and complexed species. The metals are accordingly symbolized by Mg_T and Ca_T, respectively. Comparing the top and bottom of this figure, we see that high removal of suspended solids (as well as total phosphorus, TKN, COD and filterable COD) coincides with reduction in Mg_T, whereas Ca_T remains essentially unchanged. These data indicate that Mg precipitation is primarily responsible for the observed pollutant removals and that Ca plays little or no role in the phenomenon. We can see from the figure that precipitation of 2.5 g equiv m^{-3} of Mg is sufficient to achieve good flocculation. Furthermore, since more Mg is lost at the higher pH_is, it seems likely that precipitation of $Mg(OH)_2$ is involved.

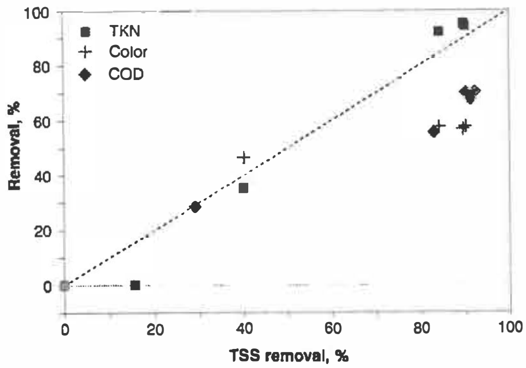

Fig. 3. Correlation between TSS separation efficiency and the removal of TKN, color and COD from alkaline wastewaters by seawater flocculation.

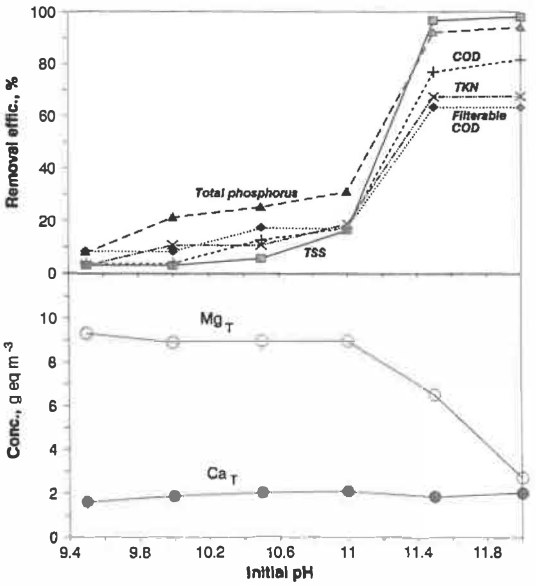

Fig. 4. Pollutant removal efficiency in relation to filterable Mg and Ca concentrations in oxidation pond effluent following seawater flocculation. Seawater concentration = 10%; initial pH was adjusted using caustic soda.

We explored the role of Mg and Ca further by examining data from the experiments with the oily wastewater. In this case, the Mg and Ca hardness was measured by EDTA titration. Since only reactive (ionic) species are measured by this technique, the metals are symbolized by Mg^{2+} and Ca^{2+}.

Residual Mg^{2+} and Ca^{2+} concentrations in the experiments with caustic are shown in relation to final pH in Fig. 5. For pHs less than 10.0, Mg^{2+} ranged from 1.3 g equiv m^{-3} at 0% seawater to 21.8 g equiv m^{-3} at 20% seawater. These concentrations were similar to calculated Mg^{2+} concentrations assuming no Mg^{2+} precipitation. Mg^{2+} decreased substantially at final pH values of 10.0 and greater. For example, at 20% seawater, Mg^{2+} was reduced from 21.8 g equiv m^{-3} at a final pH of 9.5 to 9.3 g equiv m^{-3} at a final pH of 10.3. At 5% seawater, Mg^{2+} was reduced from 5.3 to 0.1 g equiv m^{-3} between final pH values of 9.9 and 11.5. In contrast, Ca^{2+} concentrations were practically invariant through the range of final pH.

The data at the top of Fig. 5 indicate that the solubility of magnesium in the oily wastewater–seawater mixtures is controlled by pH. It is apparent that Mg^{2+} is undersaturated practically at pH less than 10.2. Above this value, Mg^{2+} varies inversely with pH in a fashion similar to that predicted by the solubility product relationship between Mg^{2+} and

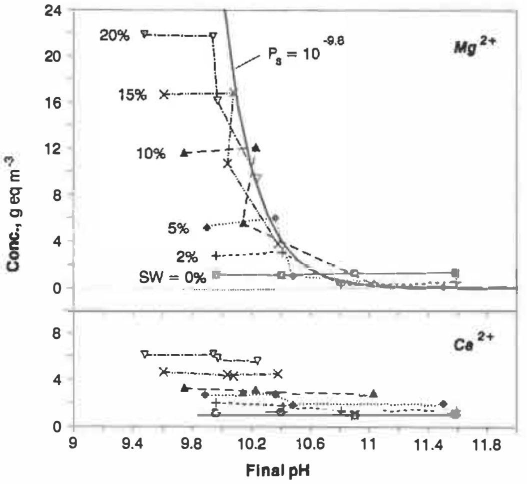

Fig. 5. pH-dependent solubility of Mg^{2+} and Ca^{2+} in mixtures of seawater and oily wastewater with caustic soda added.

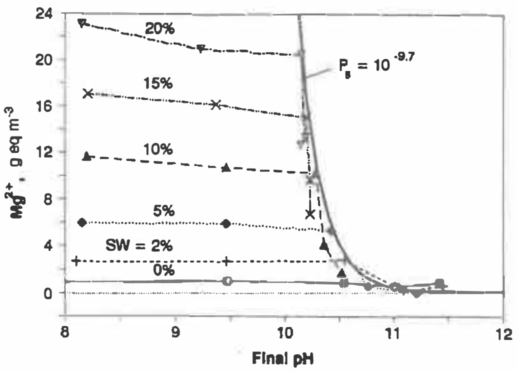

Fig. 6. pH-dependent solubility of Mg^{2+} in mixtures of seawater and oily wastewater with lime added.

OH^-. The magnitude of Mg^{2+} precipitation indicated is proportional to seawater concentration.

We calculated the conditional solubility product (P_s) for Mg^{2+} precipitation from:

$$P_s = [Mg^{2+}]\,[OH^-]^2 \qquad (2)$$

where

$[Mg^{2+}]$ = magnesium concentration measured by EDTA titrimetric procedure, in units of mol l^{-1}

$[OH^-]$ = hydroxyl ion concentration calculated from the measured pH, in units of mol l^{-1}.

The solubility of magnesium in relation to final pH is well characterized by a P_s of $10^{-9.8}$, as shown at the top of Fig. 5. This value is reasonably close to the solubility product of $10^{-9.4}$ computed by Ferguson and Vråle (1984) in their experiments with municipal wastewater–seawater mixtures.

Residual Mg^{2+} concentrations in the experiments with lime are plotted in relation to final pH in Fig. 6. We do not show the Ca^{2+} concentrations in this figure, because Ca^{2+} concentrations are increased by lime addition. Mg^{2+} appears to be undersaturated below pH 10.2. Above this value, Mg^{2+} varies inversely with pH according to a P_s of $10^{-9.7}$.

A consistent relationship between the efficiency of pollutant removal and the decrease in Mg^{2+} concentration accompanying seawater flocculation should exist if Mg^{2+} precipitation as $Mg(OH)_2$ is responsible for the observed flocculation and settling of pollutants. We tested this hypothesis using data from the oily wastewater experiments. In order to find the amount of Mg^{2+} that was removed in each experimental trial, we computed initial Mg^{2+} based on the relative volumes of seawater and wastewater, then subtracted from this quantity the measured final Mg^{2+} concentration. A plot of these data in relation to oil removal efficiency is shown at the top of Fig. 7. Oil removal efficiency was low as long as Mg^{2+} decreased by no more than 2.5 g equiv m^{-3}. At Mg^{2+} removals of 3 to 3.5 g equiv m^{-3}, oil flocculation and removal were inconsistent (6–80%). Excellent oil removal was associated with precipitation of 6 g equiv m^{-3} or more of Mg^{2+}. It would appear that precipitation of 3.5 g equiv m^{-3} of Mg^{2+} will result in good oil flocculation in most cases. In comparison, Ferguson and Vråle (1984) estimated that between 0.8 and 1.7 g equiv m^{-3} precipitate was necessary for destabilization of municipal wastewater.

We could not be as direct in estimating the amount of $Mg(OH)_2$ precipitate needed for good pollutant

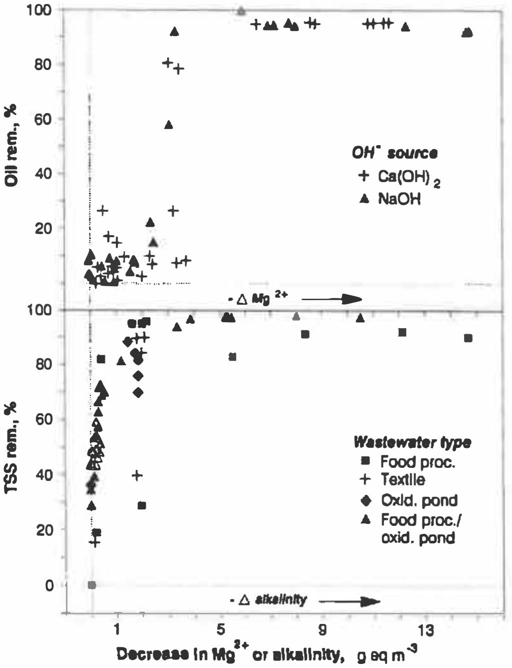

Fig. 7. Relationships between pollutant removal efficiency and the decrease in Mg^{2+} or alkalinity accompanying seawater flocculation. Top, oily wastewater; bottom, alkaline wastewaters.

removals from the alkaline wastewaters, since only a limited number of Mg measurements were made. However, alkalinity measurements were made in each trial, allowing computation of the decrease in alkalinity corresponding to each datum in Figs 2 and 3. Ca^{2+} changes little during flocculation, therefore nearly all of the observed change in alkalinity can be attributed to its reaction with Mg^{2+}.

Suspended solids removals from the alkaline wastewaters are plotted versus decrease in alkalinity at the bottom of Fig. 7. The relationship is steeply linear at low alkalinity reductions (0.5 g equiv m^{-3} or less) and plateaus at changes in alkalinity exceeding 2 g equiv m^{-3}. The latter value represents a threshold above which good flocculation is obtained.

Prediction of critical seawater concentration in relation to pH

The minimum seawater concentration needed for good flocculation will be a function of the OH^- concentration, the solubility of Mg^{2+} in equilibrium with solid $Mg(OH)_2$, and the minimum amount of $Mg(OH)_2$ that must be precipitated. Based on Fig. 7, a minimum precipitate quantity of 3.5 g equiv m^{-3} (0.00175 mol l^{-1}) is needed to obtain good flocculation of the oily wastewater, whereas a minimum precipitate quantity of 2 g equiv m^{-3} (0.001 mol l^{-1}) is needed to obtain good flocculation of the alkaline wastewaters. Assuming a closed system (i.e. no atmospheric exchange of CO_2), which is reasonable given the short time span of the process, we developed the following simple model to predict the minimum initial Mg^{2+} concentration for good flocculation:

$$[Mg^{2+}]_i = \frac{P_s}{10^{-2(K_w - pH)}} + A \qquad (3)$$

where

$[Mg^{2+}]_i$ = initial Mg^{2+} concentration needed for good flocculation in mol l^{-1}
P_s = conditional solubility product for $Mg(OH)_2$
K_w = ion product of water ($K_w = 14.1$ at 22°C or 14.0 at 25°C)
A = minimum amount of $Mg(OH)_2$ to be precipitated.

The volumetric seawater concentration needed to provide $[Mg^{2+}]_i$ is computed based on the respective Mg^{2+} concentrations in seawater and wastewater.

The predicted minimum seawater concentration for effective flocculation of the oily wastewater is plotted versus final pH in Fig. 8. We used a P_s of $10^{-9.75}$ in the computation of this relationship, which is the average of the P_s values found from data with caustic and lime. The data are in good agreement with the predicted relationship. Experimental combinations of seawater concentration and final pH lying to the left and below the line resulted generally in poor oil removals (0–59%). Combinations to the right and above the line resulted almost invariably in good to excellent removals (80–100%). As the curves and data show, the critical seawater concentration decreased in relation to final pH. A minimum seawater concentration of approx. 2% is apparently needed for good flocculation regardless of the final pH.

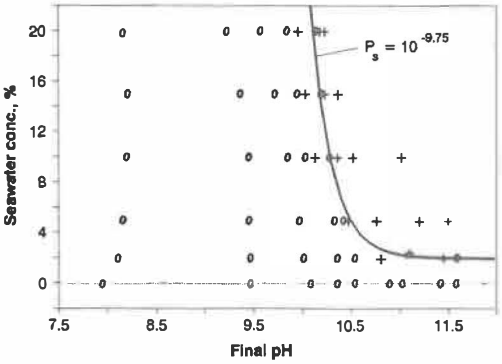

Fig. 8. Minimum seawater concentration for flocculation of oily wastewater in relation to final pH. Removal efficiency: ○, 0–59%; *, 60–79%; +, 80–100%.

Model predictions for seawater flocculation of the alkaline wastewaters are shown in Fig. 9. All but one of the data above and to the right of the curve reflect good to excellent flocculation. Most of the data below and to the left of the curve reflect poor flocculation, although there are a few points in this region representing good flocculation. Thus, the model seems somewhat conservative in this case. A better fit to the data would be expected if we had determined separately a value of P_s for the alkaline wastewater–seawater mixtures. The minimum seawater concentration needed for good flocculation was about 2%.

SUMMARY AND CONCLUSIONS

The results of the present research demonstrate that seawater flocculation is effective for demulsification of oily wastewater. They also show that flocculation of alkaline wastewaters can be accomplished

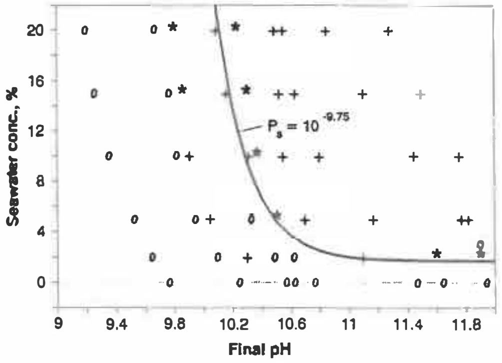

Fig. 9. Minimum seawater concentration for flocculation of alkaline wastewaters in relation to final pH. Removal efficiency: ○, 0–59%; *, 60–79% +, 80–100%.

merely by addition of seawater. The process is highly efficient for suspended solids and phosphorus removal, incidentally removes particular forms of COD and nitrogen, and was also effective against textile dyes.

Seawater serves as a source of magnesium ions, which precipitate as $Mg(OH)_2$ at high pH. Haugan (1977) demonstrated that addition of a Mg^{2+} salt by itself could duplicate the effect of seawater addition. The ability to destabilize oil emulsion and particulates, which are negatively charged, suggests that the $Mg(OH)_2$ flocs carry a positive charge in the wastewater-seawater mixtures. Proof of this hypothesis will require electrophoretic mobility studies, however. A minimum precipitate quantity of 2–3.5 g equiv m^{-3} was required to achieve good flocculation.

The solubility of Mg^{2+} in wastewater–seawater mixtures is well characterized by a conditional solubility product relationship. A simple model based on this relationship was successful in delineating the minimum seawater concentration needed for good flocculation in relation to pH. This amount varied from a minimum of 2% to a practical maximum of approx. 10%. In coastal areas, chemical cost savings realized by addition of seawater should more than offset the cost of supplying this modest quantity. Increased salinity of the final effluent should not pose a problem for ocean or estuarine disposal. Sea salt should be considered for enhancement of alkaline flocculation processes in inland regions.

Further research is needed to examine the effectiveness of seawater flocculation in removal of toxic compounds (e.g. aromatic hydrocarbons) in oily wastewaters. This could be accomplished by measuring toxicity removals in the process. Dewatering properties of the sludges produced by this process should also be determined. Fundamental studies on the interaction between $Mg(OH)_2$ floc and wastewater contaminants could yield information useful to all alkaline flocculation processes.

Acknowledgements—The present research was funded by the Engineering and Industrial Experiment Station at the University of Florida, the Research Board at the American University of Beirut and the Korea Research Council on Environmental Sciences. Experimental work at the University of Florida was performed while Dr Ayoub was a visiting professor at the Department of Environmental Engineering Sciences. The authors thank H.-G. Lee for his help in the collection and analysis of data for this research.

REFERENCES

APHA, AWWA and WPCF (1985) *Standard Methods for the Examination of Water and Wastewater*, 16th edition. American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, D.C.

API (1969) *Manual on Disposal of Refinery Wastes*, Chap. 8. American Petroleum Institute, New York.

ASTM (1986) *Annual Book of ASTM Standards*, Vols 15.04 and 0601. American Society for Testing and Materials, Philadelphia, Pa.

Ayoub G. M. and Koopman B. (1986) Algal separation by the lime–seawater process. *J. Wat. Pollut. Control Fed.* **58,** 924–931.

Ayoub G. M., Lee S.-I. and Koopman B. (1986) Seawater induced algal flocculation. *Wat. Res.* **20,** 1265–1971.

Black A. P. and Christman P. F. (1961) Electrophoretic studies of sludge particles produced in lime–soda softening. *J. Am. Wat. Wks Ass.* **53,** 737–747.

Cornwell D. A. and Bishop M. M. (1983) Determining velocity gradients in laboratory and full-scale systems. *J. Am. Wat. Wks Ass.* **75,** 470–475.

Ferguson J. F. and Vråle L. (1984) Chemical aspects of the lime seawater process. *J. Wat. Pollut. Control Fed.* **56,** 355–363.

Folkman Y. and Wachs A. M. (1973) Removal of algae from stabilization pond effluents by lime treatment. *Wat. Res.* **7,** 419–435.

Franzen A. E., Skogan V. G. and Grutsch J. F. (1972) Tertiary treatment of process water. *Chem. Engng Prog.* **68,** 65–72.

Friedman A. A., Peaks D. A. and Nichols R. L. (1977) Algae separation from oxidation pond effluents. *J. Wat. Pollut. Control Fed.* **49,** 111–119.

Haugan B. E. (1977) Effect of magnesium or polyelectrolytes as coagulant aids with chemical precipitation with lime. Norwegian Institute for Water Research. [Cited in Ferguson and Vråle (1984).]

Huang J.-C. and Hardie M. G. (1971) Treatment of refinery waste by physicochemical processes. *J. sanit. Engng Div., Proc. Am. Soc. civ. Engrs* **97,** 467–478.

Humenick M. J. and Davis B. J. (1978) High rate filtration of refinery oil wastewater emulsions. *J. Wat. Pollut. Control Fed.* **50,** 1953–1964.

Larson T. E. and Buswell A. M. (1940) Theoretical limits of the lime-soda method for water softening. *Indust. Engng Chem.* **32,** 130.

Leentvaar J. and Rebhun M. (1982) Effect of magnesium and calcium precipitation on coagulation–flocculation with lime. *Wat. Res.* **16,** 655–662.

Little R. C. and Patterson R. L. (1978) Breaking emulsions in navy bilge collection and treatment systems. *Envir. Sci. Technol.* **12,** 584–590.

Luthy R. G., Selleck R. R. and Galloway T. R. (1978) Removal of emulsified oil with organic coagulants and dissolved air flotation. *J. Wat. Pollut. Control Fed.* **50,** 331–346.

McAllister R. F. and Corcoran E. F. (1969) Chemical oceanography. In *Handbook of Ocean and Underwater Engineering* (Edited by Myers J. J., Holm C. H. and McAllister R. F.), pp. 1–17. McGraw–Hill, New York.

Nalco Chemical Co. (1979) *The Nalco Water Handbook* (Edited by Kemmer F. N.), Chap. 11. McGraw–Hill, New York.

Sadlen A. B., Pierce J. S. and Parker C. E. (1978) Development of a treatment design for oily wastewater from tankers. In *Proc. 32nd Ind. Waste Conf.*, Purdue Univ., pp. 709–715. Ann Arbor Science, Ann Arbor, Mich.

Steiner J. L., Bennett G. F., Mother E. F. and Pere L. T. (1978) Air flotation treatment of refinery wastewater. *Chem. Engng Prog.* **74,** 39–45.

Thompson C. G., Singley J. E. and Black A. P. (1972) Magnesium carbonate—a recycled coagulant. *J. Am. Wat. Wks Ass.* **64,** 11–19.

Vråle L. (1978) Chemical precipitation of wastewater with lime and seawater. *Prog. Wat. Technol.* **10,** 645.