ANDRZEJ M. DZIUBEK*, APOLINARY L. KOWAL*

INFLUENCE OF THE AERATION PROCESS ON THE STABILIZATION OF AQUEOUS SOLUTIONS OF HIGH pH VALUES

Alkaline solutions characterized by high pH values were neutralized which is a prerequisite of further uses. The most common method to achieve this involves recarbonation with carbon dioxide. In this study, pH adjustment in model and natural water solutions was obtained by aeration. The decrease in alkalinity and pH during aeration was related to its initial value. The results show that aeration can be applied for pH adjustment primarily in water renovation systems in which lime treatment in a combination with free ammonia stripping is applied.

1. INTRODUCTION

Natural waters, to say nothing of municipal sewage or industrial effluents, display a wide spectrum of chemical quality. Of the various chemical components, those characterizing the saturation of the aqueous solution desrve particular attention. Many different methods (mostly chemical) are available to minimize or eliminate the aggressive or corrosive effect of water on materials and structure by achieving a saturation state.

There are four major parameters that contribute to the lack or to the presence of stabilization, i.e., alkalinity, acidity, pH and calcium concentration. They form what is called a calcium-carbonate system referred to in specialized literature as Deffeyes diagrams and Caldwell–Lawrence diagrams [1].

One of the stabilizing methods is aeration. The process has been used so far primarily to stabilize unstable groundwaters containing excess carbon dioxide, in other words, to eliminate the aggressive action of the water, viz. the dissolution of calcium carbonate (undersaturation).

* Institute of Environment Protection Engineering, Technical University of Wrocław, 50-370 Wrocław, Poland.

Lack of stabilization is also typical of aqueous solutions, characterized by high pH values. Such solutions display the ability to precipitate calcium carbonate (supersaturation). Such are the effluents from wastewater treatment and water renovation (lime treatment) or industrial effluents, e.g., from the hydrotransport of high-calcium-content fly ash [2]. The most common method of stabilizing alkaline aqueous solutions for the needs of pH adjustment involves their recarbonation with carbon dioxide which is easily available from the flue gas stream.

During recarbonation calcium hydroxide present in the aqueous solutions reacts with dissolved carbon dioxide to give calcium carbonate particles which may be converted to calcium bicarbonate. The concentration of carbon dioxide dissolved in the water solution is influenced by the partial pressure of this compound in its gaseous phase. There is a strong relationship between carbon dioxide concentration in the gaseous mixture and the saturation time required to perform the recarbonation process.

Natural pH adjustment is found to occur during free ammonia stripping from ponds of high pH values. Absorption of airborne carbon dioxide brings about a pH drop from 11.5 to 10.0 after at least 10 days of contact [3].

The objective of the study was the stabilization of solutions of high pH. Particular attention was given to the kinetics of pH adjustment by aeration. The efficiency of pH adjustment was related to the composition of the influent stream (model and natural solutions). The method seems to be applicable to water reuse systems [4].

2. EXPERIMENTAL PROCEDURES

There were tested model and natural solutions of alkalinity and pH ranging from 50 to 650 g $CaCO_3/m^3$ and from 10.5 to 12.0, respectively. Model solutions were prepared from distilled water of different concentrations of calcium hydroxide. The actual solutions, which contained considerable amounts of calcium oxide, came from the hydrotransport of fly ash.

The samples were aerated in a 30 dm^3 volume reactor with a ceramal grate (the grate pore diameter varying from 0.02 to 0.20 mm). The aeration cycle took 10 h at a flow rate amounting to 0.3 m^3/h. Samples were collected once an hour, and then their pH values were measured and concentrations of OH^-, CO_3^{2-}, HCO_3^- and Ca^{2+} ions determined by standard methods after 1 h of sedimentation.

3. RESULTS AND DISCUSSION

The variations in the composition of the model solutions during aeration are shown in fig. 1. The aeration of slightly alkaline solutions brings about a pH drop alone. No precipitation of calcium carbonate is observed until the initial alkalinity of the solution reaches an appropriately high value.
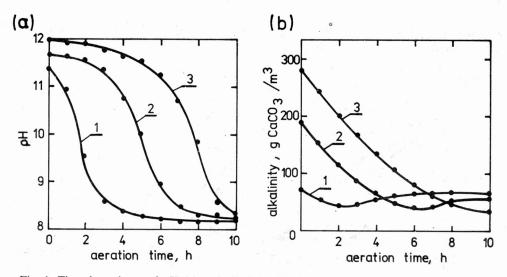
Fig. 1. Time-dependence of pH (a) and alkalinity (b) during aeration of model solutions

Irrespective of initial pH and alkalinity, the final pH value approaches 8, whereas the minimum alkalinity value (50 g $CaCO_3/m^3$) appears at pH $\approx$ 9.5. This alkalinity value corresponds with that of the water solubility of calcium carbonate. At the final stage of the aeration process, the further decrease in pH accounts for a slight dissolution of the precipitated calcium carbonate sediment.

The aeration time required to achieve stabilization of pH of the investigated model solutions varies from 4 to 8 h and depends on the initial value of alkalinity. Precipitation of calcium carbonate particles becomes noticeably intensive in the midst of the aeration process. The calcium carbonate sediment (which has been produced by the reaction of calcium hydroxide with airborne carbon dioxide) precipitates up the moment at which the saturation state, i.e., an equilibrium between water and calcium carbonate sediment, is achived. Further dissolution of calcium carbonate is insignificant, and therefore aeration takes a different course from that of the single-stage recarbonation, in which the total amount of precipitated calcium carbonate dissolves to form $Ca(HCO_3)_2$, a natural component of alkaline water.

Composition variations in high-pH natural water in the course of the aeration process are plotted in fig. 2. The aeration time required for the decrease of pH to about 8 ranges from 5 to 9 h and depends on the initial alkalinity.

The results obtained with natural water samples show very good agreement with those achived for the model solutions. Figure 3 gives examples of concentrations variations during aeration of natural water for ions contributing to water alkalinity.

Not in every instance should the pH of the water be decreased to the calcium-carbonate equilibrium. It is sometimes advisable to aim at achieving a maximum precipitation of calcium carbonate. Figure 4 relates the aeration time

A. M. DZIUBEK, A. L. KOWAL

required for pH adjustment to about 9.5 (the minimum solubility of $CaCO_3$) to the initial alkalinity of the investigated water.

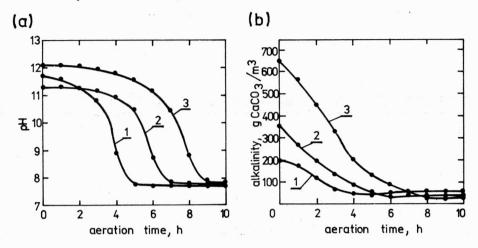**(a)**   **(b)**

Fig. 2. Time-dependence of pH (a) and alkalinity (b) during aeration of natural waters
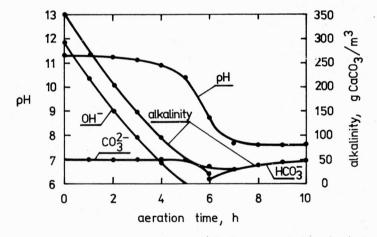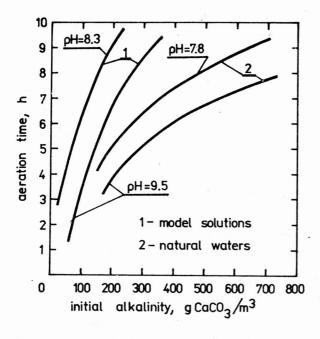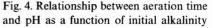

Fig. 3. Chemical composition of alkaline water during aeration

As shown by these plots, the time required to achieve complete stabilization is approximately by 2 hours longer than that required for maximum precipitation of calcium carbonate. And this is a factor that strongly affects the economy of the process. During aeration of solutions of high pH, stabilization occurs faster in natural than in model solutions of identical (or similar) initial alkalinities. This should be attributed to the precipitation of calcium carbonate which runs both easier and faster in natural waters containing a certain amount of calcium carbonate particles. These particles act as nuclei which intensify the precipitation and flocculation processes.

Fig. 4. Relationship between aeration time and pH as a function of initial alkalinity

4. CONCLUSIONS

Alkaline aqueous solutions (pH $\gg$ 11) – produced during water renovation or by some industries -- require pH adjustment prior to any uses. A widespread method of pH adjustment is recarbonation with carbon dioxide which is available from the flue gas stream.

The results of the present study show that solutions of high pH are efficiently stabilized by aeration. In the course of the aeration process, the pH of the water decreases to about 8, irrespective of the initial pH and initial alkalinity of model or natural solutions. The aeration time required for complete stabilization is longer than 4 h , and depends on the initial alkalinity of the solution, as well as on the pH desired. The aeration process yields a maximum decrease in water alkalinity to about 50 g $CaCO_3/m^3$. This value is equivalent to that of calcium carbonate solubility in water.

The calcium carbonate sediment precipitated in the course of the process flocculates easily and efficiently, displaying a good settleability. Unlike single-stage recarbonation with carbon dioxide, the aeration of alkaline solutions produces sediments which do not dissolve to form calcium bicarbonate. Stabilization of aqueous solutions of high pH by aeration should therefore be regarded as competitive with chemical methods. There is no need to use high-cost chemicals or sophisticated measuring and control systems.

Decreasing the pH level in alkaline water by aeration seems to be promising

when applied in water renovation systems involving high-lime treatment. It may be expected that the precipitating calcium carbonate particles will facilitate adsorption and co-precipitation of organics and phosphates.

REFERENCES

[1] LOEWENTHAL R. E., WIECHERS H. N. S., MARAIS G. v. R., *Softening and stabilization of municipal waters*, Water Research Commission, Pretoria 1986.

[2] DZIUBEK A. M., KOWAL A. L., *Treatment of alkaline wastewater from lignite-fried power plants*, Wat. Sci. Tech., 15 (1983), 155–162.

[3] IDELOVITCH E., MICHAIL M., *Nitrogen removal by free ammonia stripping from high pH ponds*, J. Water Poll. Control Fed., 53 (1981), 1391–1401.

[4] DZIUBEK A. M., KOWAL A. L., *Aeration process in water reuse systems*, Proc. Water Reuse Symp. IV, AWWA Research Foundation, Denver, 1987, 1183–1188.

WPŁYW PROCESU NAPOWIETRZANIA
NA NEUTRALIZACJĘ WÓD O WYSOKIM pH

Omówiono wyniki badań zmian składu wód o odczynie alkalicznym podczas procesu napowietrzania. Podano zależności efektów neutralizacji roztworów modelowych i wód naturalnych o wysokim pH od czasu napowietrzania i składu chemicznego wód. Wykazano, że przebieg i efektywność neutralizacji roztworów alkalicznych zależy głównie od ich początkowej zasadowości.

ВЛИЯНИЕ ПРОЦЕССА АЭРАЦИИ НА НЕЙТРАЛИЗАЦИЮ ВОД БОЛЬШОГО ЗНАЧЕНИЯ pH

Обсуждены результаты исследований изменений состава вод щелочной реакции во время процесса аэрации. Даны зависимости эффектов нейтрализации модельных растворов и натуральных вод большого значения pH от времени аэрации и химического состава вод. Было обнаружено, что ход и эффективность нейтрализации щелочных растворов зависит, главным образом, от их первичной щелочности.