

Using Carbon Dioxide for Alkaline Wastewater Treatment

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Abstract

Carbon dioxide capture, sequestration and disposal still poses technological and economic challenges for its substantive emission reduction. A promising cost effective method for CO₂ safe disposal is its use in neutralization of alkaline wastewater. Although this method may reduce CO₂ emission by 1 ton/year for every 1 ton /day of alkaline wastewater treated, yet its economics, environmental and safe operation outweigh the use of other mineral or organic acids. This paper critically discusses comparative studies on the economics and environmental benefits of using CO₂ for wastewater neutralization. The paper presents experimental neutralization curves under different conditions of CO₂ flow rates, mixing and initial CO₂ partial pressure. The results show the technical feasibility of using CO₂ as a neutralizing agent.

Introduction

Wastewaters can be classified as: Municipal wastewaters and industrial wastewaters. Municipal wastewaters are produced by domestic activities of the community while industrial wastewaters result from spills, leaks, product washing, process cooling wastewaters and sanitary activities in a particular industrial facility.

Wastewaters Characteristics

Wastewaters characteristics vary widely from industry to industry and from municipality to another. Obviously, the specific characteristics will affect the treatment technology chosen for use in meeting discharge requirements. These characteristics are shown in Table 1.1

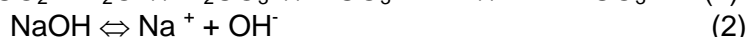
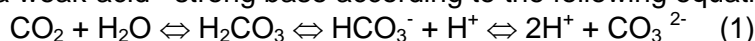
Table1.1 Wastewaters Characteristics

Property	Characteristic	Example	Size or Concentration
Solubility	Soluble	Sugar	100 gm/L
	Insoluble	PCB	< 1 mg/L
Stability, biological	Degradable	Sugar	
	Refractory	DDT, metals	
Solids	Dissolved	NaCl	< 10 ⁻⁸ m
	Colloidal	Carbon	10 ⁻⁶ - <10 ⁻⁹ m
	Suspended	Bacterium	>10 ⁻⁶
Organic Inorganic pH	Carbon	Alcohol	
	Inorganic	Cu ⁺²	
	Acidic	HNO ₃	
	Neutral Basic	Salt (NaCl) NaOH	1-12
Temperature	High-low	Cooling	>5°
		Heat exchange	>30°
Toxicity	Biological effect	Heavy metals Priority compounds	Varies
Nutrients	N	NH ₃	varies
	P	PO ₄ ³⁻	

Alkaline wastewater is produced from various industries such as the iron and steel making industries, textile and dyeing industries, pulp and paper industries, to name a few. Such industries generate highly alkaline wastewater (11.4 pH average), which must be neutralized before it can be discharged or sent for further biological treatment. Traditionally, sulfuric or hydrochloric acids were used for neutralization. These strong mineral acids pose difficulties in process control, handling, maintenance of equipment, and chemical cost. Moreover, accurate pH control using these mineral acids is often difficult to achieve. Initially the pH remains fairly constant during acid dosing, however, there is a sudden change near or at the neutral point and the pH drops drastically even after the addition of small amounts of the acid. As an alternative neutralizing agent, CO₂ offers the following advantages over mineral acids:

1. CO₂ is not a highly toxic material and is safer to personnel and requires no special protective equipment to handle, less safety measures for handling, emergency spill response, or special monitoring of deliveries to detect leaks.
2. Due to its natural buffering action, CO₂ cannot reduce the pH below 5, even if over dosing occurs. Thus it provides improved process control, where pH drop with CO₂ addition occurs more gradually than with mineral acids, making accurate control inherently easier.
3. The neutralization process becomes environmentally friendly since CO₂ does not produce residual anions such as sulfate and chloride and even friendlier if recycled CO₂ from flue gases were used.
4. Replacement of an existing mineral acid neutralization system or the erection of a new CO₂ system can be achieved at a lower cost. Commercial CO₂ is typically about the same price as sulfuric acid, though its consumption is 1.5 times less, and about half the price of that of hydrochloric acid. The capital and operating costs of a CO₂ system are lower than that of an equivalent mineral acid system and easier and cheaper to modify [1].

The findings of using CO₂ as neutralizing agent are obtained from pilot and industrial scale applications [1,2,3,4]. This use of CO₂ can be a contribution to CO₂ abatement technologies. Neutralizing using CO₂ is best suited for treatment of industrial flue gases containing CO₂ and in situ alkaline wastewater. Pilot plant studies [] showed that this method may reduce CO₂ emission by 1 ton/year for every 1 ton/day of alkaline wastewater treated. The economic viability of the CO₂ neutralizing method depends on several factors; of which: 1) the concentration of CO₂ in the emission source, 2) the level of alkalinity and the availability of wastewater relative to the emission source, and 3) temperature. Combustion of fossil fuels with stoichiometric air produces an exhaust gas containing approximately 9% CO₂ for hydrocarbon fuels and about 21% in combustion of coal. Using excess air reduces CO₂ concentration according to the amount of excess air. Further development of this technology requires modeling and simulation in order to investigate and predict conditions that lead to the optimum use of CO₂ as neutralizing agent. Model prediction and interpretation of process behavior requires a quantitative understanding of CO₂ system kinetics and thermodynamics. In this study, a neutralization simulation model was developed incorporating the mass transfer of CO₂ from the gas to the liquid phase, and the subsequent dissociation of carbonic acid. The neutralization process was modeled as a weak-acid –strong base according to the following equations:



The aqueous phase-carbon dioxide gas exchange process was described by the "Stagnant two-film" [5] and "Surface renewal" [6] models.

Development of the Neutralization Model

The two-step neutralization of sodium hydroxide solution (representing the alkaline wastewater) by bubbling of a water-saturated stream of CO₂ gas into it, is shown schematically in Fig.(1).

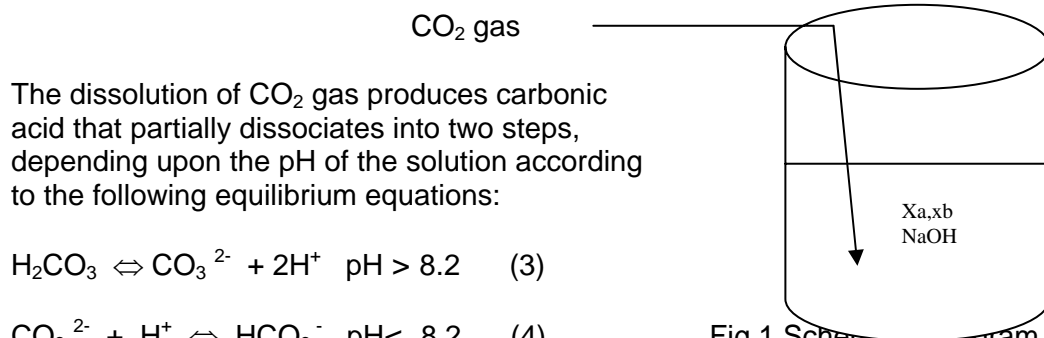
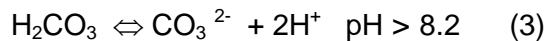


Fig.1 Schematic Diagram of Neutralization Process

The dissolution of CO₂ gas produces carbonic acid that partially dissociates into two steps, depending upon the pH of the solution according to the following equilibrium equations:



The stoichiometric (or apparent) dissociation Constant for reaction (3) is defined by the following equation:

$$K_3 = \frac{[\text{CO}_3^{2-}][\text{H}^+]^2}{[\text{H}_2\text{CO}_3]} \quad (5)$$

Similarly:

$$K_4 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_3^{2-}]} \quad (6)$$

The dissociation of water at 25 C is given by:

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \quad (7)$$

K₃ and K₄ expressed in terms of concentration rather than activities would not introduce an error in excess of a few percent if their ratios to the ratios of concentrations is 10⁻³ or less [7]. Thus for simplicity concentrations will be used instead of activities in the formulation of the model.

The dissociation constants of carbonic acid starting from a pH of 4.4 are given by:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (8)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (9)$$

Therefore $K_3 = K_1K_2$ and $K_4 = 1/K_2$

Where:

$$\text{p}K_1 = -14.8435 + 3.40471 \cdot 10^3 / T + 3.2786 \cdot 10^{-2} T \quad T(\text{temperature (K)})$$

$$\text{p}K_2 = -6.4980 + 2.90239 \cdot 10^3 / T + 2.379 \cdot 10^{-2} T$$

Material Balance

The dynamic mathematical model is developed by writing unsteady state total and component material balances of cations and anions around the neutralization tank. Assuming that the tank is perfectly mixed, that the volume remains essentially constant, and that the system is operated isothermally at 25° C, we have, for the first dissociation step:

$$x_a = [\text{H}_2\text{CO}_3]_1 + [\text{CO}_3^{2-}] \quad (10)$$

$$x_b = \text{Na}^+ \quad (11)$$

$$Vdx_a/dt = Fx_a \quad (12)$$

$$Vdx_b/dt = 0 \quad (13)$$

Electro neutrality Balance

$$2\text{H}^+ + 2\text{Na}^+ = \text{CO}_3^{2-} + 2\text{OH}^- \quad (14)$$

Similarly for the second dissociation step the material and electro neutrality balances yield:

$$[\text{H}_2\text{CO}_3]_1 = [\text{H}_2\text{CO}_3]_2 + [\text{HCO}_3^-] \quad (15)$$

$$\text{H}^+ + 2\text{Na}^+ = \text{CO}_3^{2-} + \text{HCO}_3^- \quad (16)$$

CO₂ Transfer across the Gas-Liquid Interface

Since CO₂ is sparingly soluble in an aqueous phase, the resistance to mass transfer is essentially localized in the liquid boundary layer or film. Accordingly, a general expression for the rate of CO₂ transfer (F_{CO_2}) across the interface is given by the equation:

$$F_{\text{CO}_2} = -uA(x_a - K_H p_{\text{CO}_2}) \quad (17)$$

Where: u = CO₂ gas bubbling velocity; p_{CO_2} = CO₂ partial pressure in equilibrium with concentration x_a in the solution, A = contact area and K_H is Henry's law constant for CO₂ given as a function of temperature by [9]:

$$\ln K_H = -5.747 \cdot 10^{-2} + 2.154 \cdot 10^{-4}/T - 1.477 \cdot 10^{-4}/T^2 + 89.89 \ln T \quad (18)$$

By a series of simplifications and substitutions, Eqs.(5)-(18) are solved sequentially and simultaneously together with the definition of pH as:

$$\text{pH} = -\log[\text{H}^+] \quad (19)$$

to give the model equation relating the pH with time during the neutralization of NaOH solution by bubbling CO₂ gas in a perfectly mixed tank.

Experimental Setup

The apparatus used in the neutralization experiments is a Metrohm SM Titrino 702 series 29, in which CO₂ gas is bubbled into a stirred aqueous solution of NaOH and the pH is measured continuously with time. The temperature, pressure, solution volume and initial pH were kept constants at 25 °C, 1 atm., 125mL and 9.35 respectively. The following variable were varied one at a time, keeping the others constants:

- CO₂ gas velocity (by varying the bubbler's porosity).
- Stirrer speed.
- CO₂ gas flow rate.
- CO₂ composition.

Base values of these variables were porosity =3 (highest velocity), stirring speed = 4 rpm, and 0.1 L/min (at 25 C and 1 atm.) CO₂ gas flow rate.

Results and Discussion

a) Simulation Results

The set of model equations are solved using Polymath (ODE solver) software using the parameter values shown in Table 1

Parameter	Value
$x_{bo}\{Na^+\}$	10 –4 M
V	0.1 L
F	1L/min
Temperature	25° C
p_{CO_2}	0.962 atm

Fig.2 shows the simulated neutralization curves for various conditions of CO₂ transfer across the interface. Curve1 is the neutralization curve for negligible mass transfer resistance across the liquid film. This curve is similar to the general polyprotic acid-strong base neutralization systems [7] and shows the following characteristics:

1. The two alkalinity end points at pH = 8.2 and pH = 4.4.
2. pH range at which the drastic change of pH occurred is smaller than strong acid-strong base system.

Curves 2 and 3 show similar characteristics; though it takes longer time to reach a desired pH. Curve2 is obtained using a CO₂ bubbling velocity higher than that of curve3 and both approach curve1 as the bubbling velocity is increased. This can be explained by considering Eqs(12) and (17) from which we obtain:

$$x_a = K_H p_{CO_2} / \{(F/Au) + 1\}$$

Clearly that as the CO₂ gas bubbling velocity and the speed of the mixer are increased, the term F/Au approaches zero and the carbonic acid concentration x_a approaches the saturation value of $K_H p_{CO_2}$.

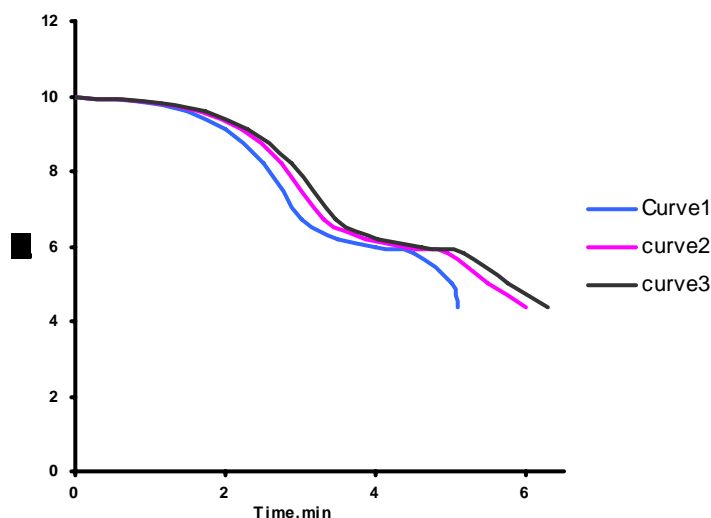


Fig.2 Simulated Neutralization Curves

b) Experimental Results

Fig.(3) shows the effect of CO₂ gas velocity on the neutralization of NaOH in which the first alkalinity end point is clearly indicated and is reached in a shorter time as the CO₂ gas bubbling velocity is increased.

Fig.(4) shows the effect of stirrer speed on the position of the alkalinity end point; where as the stirring speed is increased, the end point was reached in a shorter time.

Fig.(5) shows the effect of CO₂ gas flow rate on the end point, producing similar effects. The results show that the gas-liquid mass transfer coefficient is increased by the combined increase in gas velocity and flow rate and by the degree of mixing in the vessel. In effect, the neutralization reaction becomes the controlling step and consequently the end point is reached in a shorter time. The results agree with the simulated results; except that the second neutralization end point was not as distinct. For the conditions studied, this may be attributed to the formation of acidic buffer solution that resists change in pH no matter how much CO₂ is added.

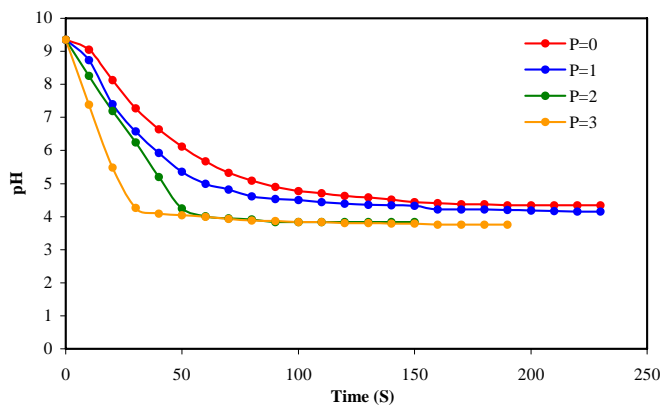


Fig.3 Variation of Porosity

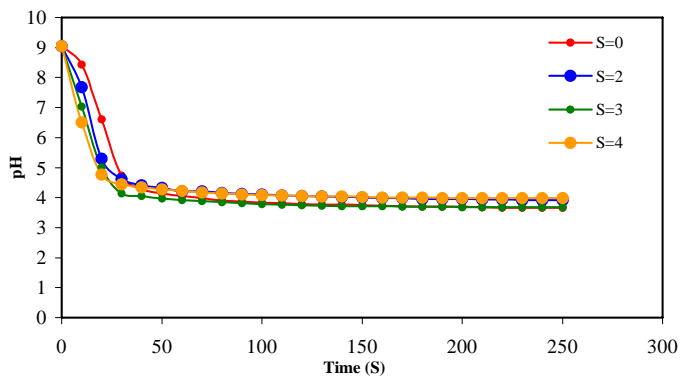


Fig.4 Variation of Stirrer Speed

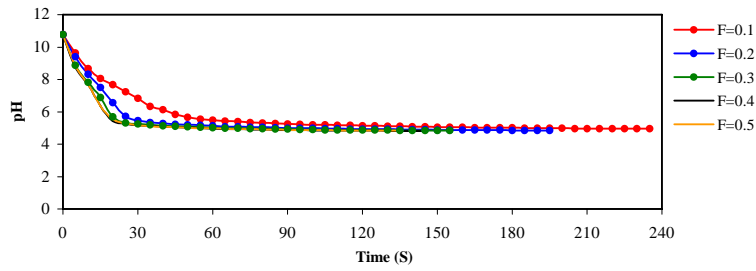


Fig.5 Variation of CO₂ Flow Rate

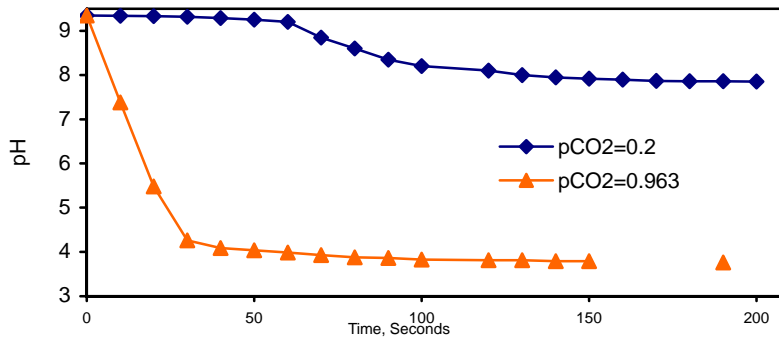


Fig. 6 Effect of CO₂ Partial Pressure

Fig. 6 compares the effect of CO₂ partial pressure on the neutralization curve at the optimum conditions of mixing. Clearly the decrease in CO₂ partial pressure elongates the duration to reach a specific pH.

Conclusions

In this study, modeling, simulation and experimental work on CO₂ neutralization of alkaline water has been presented. The following conclusions may be drawn from this study:

1. The simulated neutralization curve agrees with the general curve of polyprotic acids strong base neutralizations.
2. The neutralization curve shows clearly the gradual two end points regions where the pH control becomes easier than when using strong mineral acids.
3. Experimental results agreed reasonably with the simulated ones.
4. Mass transfer limitations across the CO₂gas-liquid interface could be significant and calls for careful consideration when designing the equipment for dosing CO₂ gas into the alkaline solution.

5. Reducing the CO₂ partial pressure increased the time necessary to reach a certain pH.
6. The CO₂ neutralization method could be economically viable in case of availability of alkaline wastewater in proximity of the CO₂ emission source.
7. Further investigation of the method using natural alkaline salts as bases for neutralization is recommended. This method would be promising especially if taxing CO₂ emissions at \$26/t as suggested by the UK Department of Trade and Industry [10].

References

[1] Commonwealth of Massachusetts Executive Office of Environmental Toxics Reduction, "Case Study No. 33 : Use of CO₂ to replace sulfuric acid to pH adjustment", Sep. 1995. [http:// www.nben.org](http://www.nben.org).

[2] Choi, S.K., Ko, K.S. and Chun, H.D., "Utilization of CO₂ for neutralization of alkaline wastewater". Report submitted to Research Institute of Industrial Science and Technology, South Korea.

[3] Nishimura, S. and Yoda, M., "Effect of decarbonation on alkaline reduction in two phase UASB process". Water Science and Technology, v34, n5-6, 1996.

[4] Gomolka, E. and Gomolka, B., "Application of disk aerators to recarbonation of alkaline wastewater from wet gasification of carbide". Water Science and Technology, v24,n7, 1991.

[5] Liss, P.S. and Slater, P.G., "Flux of gases across air-sea interface". Nature, 247,5438, 1974.

[6] Danckwerts, P.V., "Significance of liquid –film coefficients in gas absorption". Ind.Eng.Chem., v43,n3,1951.

[7] Wallace, S.B., "Principles of physical chemistry". Appleton-Century-Crofts, Inc., 1958.

[8] Cai, W.J. and Wang, Y., "The chemistry, fluxes and sources of CO₂". Oceanog.,v43, 1998.

[9] Weiss, R.F., "CO₂ in water and sea water: the solubility of an ideal gas". Mar.Chem, v2, 1974.

[10] Carbon Capture Boost, Chemical & Engineering News,85, February 2006.