CHAPTER 3

Neutralization

“Neutralization” can be defined for usage in this book as the treatment of industrial waste so that it is neither too acidic nor too alkaline for safe discharge. There are several possible reasons that an industry neutralized its wastewater during the twentieth century and will continue to do so:

1. To render it compatible with the treatment of municipal sewage when joint treatment is practiced
2. To continue reason no. 1; more specifically, to make certain that its pH does not kill or otherwise inactivate the microorganisms that are being used to biologically oxidize the organic matter content
3. To prevent corrosion of pipelines and equipment leading from the industry to its ultimate destination
4. To comply with municipal or other governmental ordinances of excessive acid or alkaline conditions in sewers or receiving waters.
5. To continue reason no. 4; more specifically, to make certain that the waste discharge pH does not kill fish or otherwise affect other organisms in receiving waters

Excessively acid or alkaline wastes should not be discharged into a receiving stream without treatment. A stream even in the lowest classification—that is, one classified for waste disposal and/or navigation—is adversely affected by low or very high pH values. This adverse condition is even more critical when sudden slugs of acids or alkalis are imposed upon the stream.

At a pH of only 6.5, trout of three species (brook, brown, and rainbow) have shown significantly reduced hatching of eggs and growth. When the pH is lowered to 5.5, bass, walleyed pike, and rainbow trout have been reported to be eliminated (Boyle 1981), as have declines in trout and salmon populations. Below pH 5, most fish are unable to survive. This low pH causes female fish to deter laying of their eggs, and if laid, the fish are very sensitive in the egg, larval, and fish frog stages. Low pH can interfere with the salt balance that freshwater species of fish need to maintain in their body tissues and blood plasma. Acid ioniges or other entities activate many metals already present, such as aluminum, which can be toxic to the fish even at pH values normally considered safe.

There are many acceptable methods for neutralizing overacidity or overalkalinity of wastewater, such as: (1) mixing wastes so that the net effect is a near-neutral pH; (2) passing acid wastes through beds of limestone; (3) mixing acid wastes with lime slurries or dolomitic lime slurries; (4) adding the proper proportions of concentrated solutions of caustic soda (NaOH) or soda ash (NA_2CO_3) to acid wastes; (5) blowing waste boiler-flue to alkaline wastes; (6) producing CO_2 in alkaline wastes; and (7) adding sulfuric acid to alkaline wastes.

The material and method used should be selected on the basis of the overall cost, as material costs vary widely and equipment for using various agents will differ with the method selected. The volume, kind, and quantity of acid or alkali to be neutralized are also factors in deciding which neutralizing agent to use.

In any lime neutralization treatment, the waste engineer should establish a minimum acceptable effluent pH and allow adequate reaction time for an acid effluent to reach this minimum pH. This will usually save considerable unnecessary expense (Lewis and Yost 1950). In many cases, a mill can cut down on neutralization costs by providing sufficient detention time and sacrificing some efficiency in subsequent biological treatment (if used). During storage of alkaline wastes in contact with air, CO_2 will slowly dissolve in the waste and lower the pH. However, detention time alone, within feasible limits, will not effect as low a final pH as can be obtained by the use of neutralizing chemicals. Because biological treatment is more efficient at pH values nearer neutrality, prior neutralization by chemicals renders such treatment more effective.

Mixing Wastes

Mixing of wastes can be accomplished within a single plant operation or between neighboring industrial plants. Acid and alkaline wastes may be produced individually within one plant and proper mixing of these wastes at appropriate times can accomplish neutralization (Figure 3.1), although this usually requires some storage of each waste to avoid slugs of either acid or alkali.

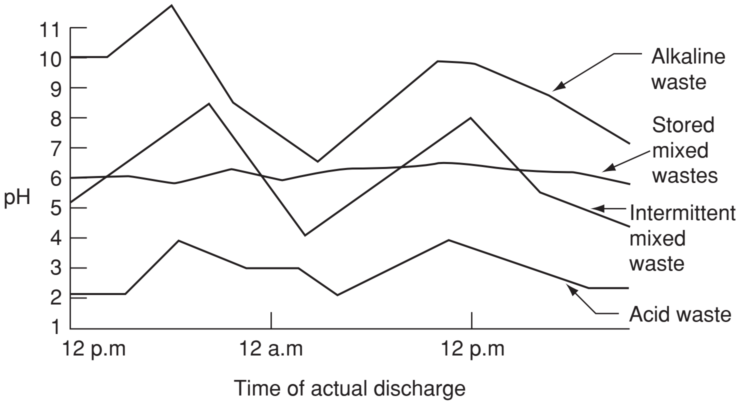


FIGURE 3.1. Neutralization accomplished by mixing of wastes.

If one plant produces an alkaline waste that can be pumped conveniently to an area adjacent to a plant discharging an acid waste, an economical and feasible system of neutralization results for each plant. For example, a building-materials plant producing an alkaline (lime and magnesia) waste pumps the slurry, after some equalization, about one-half mile to mix with the effluent from a chemical plant, producing an acid waste. The neutralized waste resulting from this combination is more readily treatable for final disposal, and both plants thereby solve problems in economics, politics, and engineering. In another instance, Hyde (1965) reports the use of a 500,000-gallon reservoir ahead of an anaerobic digestion pond to mix various types of plant wastes before treatment. The resulting pH of the reservoir effluent ranged from 6.5 to 8.5.

Limestone Treatment for Acid Wastes

Passing acid wastes through beds of limestone was one of the original methods of neutralizing them (Gehm 1944; Reidl 1947). The wastes can be pumped up or down through the bed, depending on the head available and the cost involved, at a rate of about 1 gallon/min (gpm) per square foot (ft^2) or less. Neutralization proceeds chemically according to the following typical reaction:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$$

The reaction will continue as long as excess limestone is available and in an active state. The first condition can be met simply by providing a sufficient quantity of limestone; the second condition is sometimes more difficult to maintain. A sulfuric acid solution must be diluted to an upper limit of about 5% and applied at a rate less than 5 gpm/ft^2 to avoid fouling the bed. According to Jacobs (1951), no attempt should be made to neutralize sulfuric acid above 0.3% concentration or at a rate of feed less than 1 gpm/ft^2 because of the low solubility of calcium sulfate. Excessive acid will precipitate the calcium sulfate and cause subsequent coating and inactivation of the limestone.

Disposing of the used limestone beds can be a serious drawback to this method of neutralization, because the used limestone must be replaced by fresh limestone at periodic intervals, with the frequency of replacement depending on the quantity and quality of acid wastes being passed through a bed. When there are extremely high acid loads, foaming may occur, especially when organic matter is also present in the waste.

Lime-Slurry Treatment for Acid Wastes

Mixing acid wastes with lime slurries is an effective procedure for neutralization (Hoak 1944; Rudolfs 1943a,b; Smith 1943). The reaction is similar to that obtained with limestone beds. In this case, however, lime is used up continuously because it is converted to calcium sulfate and carried out in the waste. Though slow acting, lime possesses a high neutralizing power and its action can be hastened by heating or oxygenating the mixture. It is relatively inexpensive, but in large quantities, cost can be an important factor.

Hydrated lime is sometimes difficult to handle, because it tends to arch, or bridge, over the outlet in storage bins and possesses poor flow properties, but it is particularly adaptable to neutralization problems involving small quantities of acid waste, as it can be stored in bags without special storage facilities.

In an actual case (Dickerson and Brooks 1950), neutralization of nitric and sulfuric acid wastes in concentrations up to about 1.5% (in the case of sulfuric acid) was accomplished satisfactorily by using a burned dolomitic stone containing 47.5% CaO, 34.3% MgO, and 1.8% $CaCO_3$. The concentration of acid was limited to the stated 1.5%, at least in part, because of the absence of dilution water to vary the percentage. This stone provided the additional advantage of holding residual sulfation to a minimum, an impossibility with any of the high-calcium limes (Jacobs 1947).

Caustic-Soda Treatment for Acid Wastes

Adding concentrated solutions of caustic soda or sodium carbonate to acid wastes in the proper proportions results in faster, but more costly, neutralization. Smaller volumes of the agent are required, because these neutralizers are more powerful than lime or limestone. Another advantage is that the reaction products are soluble and do not increase the hardness of receiving waters. Caustic soda is normally bled into the suction side of a pump discharging acid wastes. This method is suitable for small volumes, but for neutralizing large volumes of acid wastewater, special proportioning equipment (see Chapter 2) should be provided, as well as a suitably sized storage tank for the caustic soda with a multiple-speed pump for direct addition of the alkali to the flow of acid wastes.

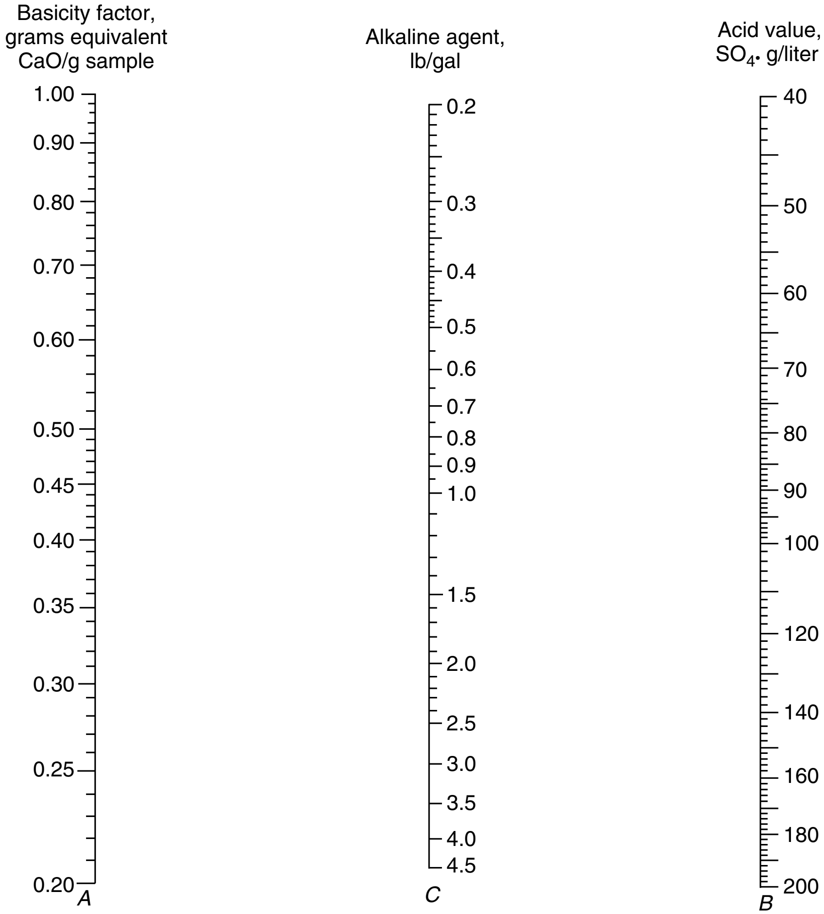
We have now discussed four methods of neutralizing acid wastes. Before moving on to alkaline wastes, compare the "basicity" and costs of the acid-neutralizing methods and agents (Table 3.1).

TABLE 3.1
Cost Comparison of Various Alkaline Agents[a]

Chemical	*Cost, $/Ton (approx.)*	*Basicity Factor*[b]	*Cost, $/Ton of Basicity*
NaOH (78% Na_2O)	106	0.687	154
Na_2CO_3 (58% Na_2O)	57	0.507	112
MgO	83	1.306	64
High-calcium hydrated lime	14	0.710	20
Dolomitic hydrated lime	14	0.912	15
High-calcium quicklime	11	0.941	12
Dolomitic quicklime	11	1.110	10
High-calcium limestone	4	0.489	8
Dolomitic limestone	4	0.564	7

[a] Based on 1954 cost quotations.
[b] A measure of the alkali available for neutralization (grams of equivalent CaO/per/gram).
Adapted from Hoak (1950).

Because the basicity factor, as shown in Table 3.1, is one of the vital factors in selecting a neutralizing agent, Hoak (1958) provides not only a method for computing this factor but also a nomograph for calculating the pounds of neutralizing agent required per gallon of waste (Figure 3.2). He determines the acid value by titrating a 5-ml sample of sulfuric acid waste with an excess amount of 0.5 *N* NaOH and back-titrating with 0.5 *N* HCl to a phenolphthalein endpoint. The basicity factor of the lime (or neutralizing agent) is determined by titrating a 1-g sample of alkaline agent with an excess of 0.5 *N* HCl, boiling the sample for 15 minutes, and back-titrating with 0.5 *N* NaOH to the phenolphthalein endpoint. The acid value (line B in Figure 3.2) and basicity factor (line A in Figure 3.2) are then connected in Hoak's nomograph to find the pounds of alkaline agent required per gallon of acid waste (line C in Figure 3.2).



Connect scales A and B with a straight edge and read the result on scale C

FIGURE 3.2. Nomograph for treatment of acid wastes: a chart for determining the amount of alkaline agent needed (adapted from Hoak 1958).

When sodium hydroxide is used as a neutralizing agent for carbonic and sulfuric acid wastes, the following reactions take place:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3,$$

carbonic acid waste

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O;$$

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + HOH,$$

sulfuric acid waste

$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + HOH.$$

Both these neutralizations take place in two steps and the end-products depend on the final pH desired. For example, one treatment may require a final pH of only 6, and thus, $NaHSO_4$ would make up the greater part of the products; another treatment may require a pH of 8, with most of the product being Na_2SO_4.

We shall now take up the subject of neutralization of alkaline wastes.

Using Waste Boiler-Flue Gas

Blowing waste boiler-flue gas through alkaline wastes is a relatively new and economical method for neutralizing them. Most of the experimental work has been carried out on textile wastes (Beach and Beach 1956; Nemerow 1956; Rudolf 1943; Steele 1954; *Treatment of Alkaline Sulfur Dye Waste with Flue Gas* 1956). Well-burned stack gases contain approximately 14% carbon dioxide. CO_2 dissolved in wastewater will form carbonic acid (a weak acid), which in turn reacts with caustic wastes to neutralize the excess alkalinity as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3,$$

flue gas   wastewater   carbonic acid

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H2O,$$

carbonic acid   caustic soda in wastewater   soda ash

$$H_2O$$

$$H_2CO_3 + Na_2CO_3 \rightarrow 2NaHCO_3 + H_2O.$$

Excess carbonic acid   soda ash in waste   sodium bicarbonate in waste

The equipment required usually consists of a blower placed in the stack, a gas pipeline to carry the gases to the waste-treatment site, a filter to remove sulfur and unburned carbon particles from gases, and a gas diffuser to disperse the stack gases in the wastewater. Stack gases evolve hydrogen sulfide from wastewater that contains any appreciable quantity of sulfur, and this H_2S must be burned, absorbed, or vented positively to the upper atmosphere to prevent nuisance conditions.

Carbon Dioxide Treatment for Alkaline Wastes

Bottled CO_2 is applied to wastewater in much the same way as compressed air is applied to activated-sludge basins. It neutralizes alkaline wastes on the same principle as boiler-feed gases (i.e., it forms a weak acid [carbonic acid] when dissolved in water) but with much less operating difficulty. The cost may be prohibitive, however, when the quantity of alkaline wastes is large. A textile mill (Nemerow 1956) producing about 6 million gallons/day of alkaline waste studied the practical aspects of this method and found that installation of the equipment necessary to provide bottled CO_2 would cost about $150,000 and the power and fuel to generate it about $275/day—a considerable expense, even for so large a plant.

Producing Carbon Dioxide in Alkaline Wastes

Another way to produce carbon dioxide is to burn gas underwater. This process is called *submerged combustion* and has been used in the disposal of nylon wastes (Remy and Lauria 1958) to neutralize the waste before biological treatment. In pilot-plant studies, the researchers (Remy and Lauria 1958) investigated submerged combustion on a continuous basis, using an evaporation vessel, a burner with flame jets submerged below the waste surface in the vessel, a bustle in which air and natural gas were mixed to form a combustible mixture, and other equipment to measure air, gas, and waste flows and the weight of waste volatilized during each run. A schematic drawing of the submerged-combustion plant used is shown in Figure 3.3. Researchers concluded that submerged combustion, rather than aeration, should be used to treat part of the plant waste, for

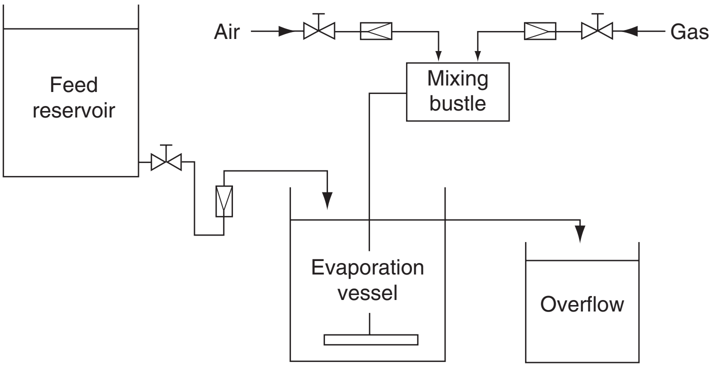


FIGURE 3.3. Submerged-combustion pilot unit as used by Remy and Lauria (1958).

economic reasons. (The researchers in this case, however, were primarily concerned with stripping toxic materials from the waste, rather than with neutralizing it.) Krofchak (1962) describes this method of neutralization and suggests its use for spent pickle liquors and spent electrolytes from nickel refining. CO_2 may also be produced by fermentation of an alkaline, organic waste; the resulting pH is thus lowered. EbaraInfilco, Ltd. in 1965 patented such a process for fermenting alkaline beet-sugar wastes with yeast; the CO_2 produced can be used for neutralization and the excess yeast as forage.

Sulfuric Acid Treatment for Alkaline Wastes

The addition of sulfuric acid to alkaline wastes is a fairly common, but expensive, means of neutralization. Sulfuric acid can cost as much as 2 or 3 cents per pound, although it may be as low as 1 cent per pound in large quantities. Storage and feeding equipment requirements are low as result of its great acidity, but it is difficult to handle because of its corrosiveness. The neutralization reaction that occurs when it is added to wastewater is as follows:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

wastewater sulfuric acid as neutralizer resulting neutral salt

A titration curve of the alkaline waste neutralized with various amounts of H_2SO_4 is helpful to ascertain the quantities of acid required for neutralization to definite pH values and the relevant costs. Figure 3.4 represents the titration curve of an actual mixed alkaline waste in Niagara Falls, New York.

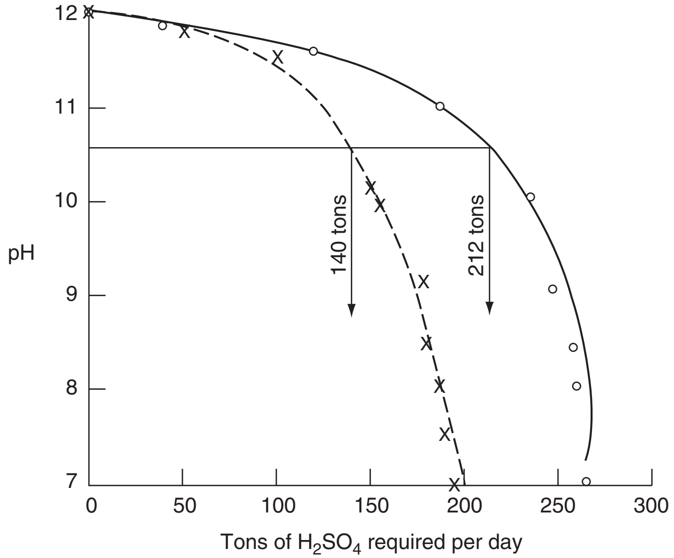


FIGURE 3.4. Acid required to neutralize industrial wastes in sewer.

During most of the twentieth century, a widely held opinion was that a high pH—say, 10 or higher—would so adversely affect biological oxidation that acid neutralization would be required. In some cases this may be true, but an industrial waste with a pH of 10 could be effectively degraded aerobically (biologically) without neutralization (Emerson and Nemerow 1969). The reader can readily realize the great potential savings in capital and operating costs of omitting the neutralization step here and in other cases of high alkalinity.

Acid-Waste Utilization in Industrial Processes

In some situations, it may be possible to use acid wastes to get the desired result in industrial processing: wash, cool, or neutralize products. For example, Dillon (1967) reports the use of acid-mine drainage water for cleaning raw coal. Mine wastewater occurs in large quantities in the coal industry. These waters are usually acidic and contain sulfates of iron and aluminum; if they are used to wash raw coal, neutralization results, because coal contains calcium and magnesium carbonates. Dillon (1967) describes the treatment of 600 tons of raw coal per hour, with an average of 225 gpm of mine wastewater. The pH of the mine water is thereby raised from 3.0 to neutrality.

Example of Twentieth-Century Practice of Neutralization

Drury (1999) found that the unusual use for pH neutralization of anaerobic digestion of acid mine drainage wastewater could raise the pH of the wastewater, as well as having other contaminant removal effects. He reported that adding whey to the anaerobic substrate reactor improved the long-term treatment efficiency for pH neutralization, alkalinity production, and sulfate, iron, zinc, and manganese removal.

Effluent pH—according to Drury (1999)—from the reactor with whey addition was relatively constant at 6.5.

Review Questions

1. Name seven major methods of neutralizing both acid and alkaline wastes.
2. What are the four major factors to be considered when neutralizing wastes?
3. What effect can the storage of alkaline wastes have on pH and resulting neutralization?
4. Under what conditions would you select mixing of wastes as a solution to neutralization?
5. When would you use limestone beds or filters for acid wastes?
6. What is the advantage of using lime slurry rather than limestone beds for neutralization?
7. When would you use NaOH or Na_2CO_3 for neutralization?

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