FS-PRE-004

TECHNOLOGY FACT SHEETS
FOR EFFLUENT TREATMENT PLANTS
ON TEXTILE INDUSTRY

pH NEUTRALIZATION

SERIES: PRE-TREATMENTS

TITLE	**pH NEUTRALIZATION (FS-PRE-004)**
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INDITEX

pH NEUTRALIZATION (FS-PRE-004)

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INDEX

1. INTRODUCTION

Many industrial wastes contain acidic or alkaline materials that require neutralization prior to discharge to receiving waters or prior to chemical or biological treatment. (Eckenfelder, 2000)

Neutralization **is the process of adjusting the pH of water through the addition of an acid or a base**, depending on the target pH and process requirements. Most part of the effluents can be neutralized at a pH of 6 to 9 prior to discharge.

In chemical industrial treatment, neutralization of excess alkalinity or acidity is often required. One of the critical items in neutralizing the water is to determine the nature of the substances that cause acidity and alkalinity. This is generally achieved in laboratory scale experiments by preparing titration curves showing the quantity of alkaline or acidic materials necessary to adjust the pH of the target wastewater (Goel, 2005).

There are three critical components of any pH control system: **mixing intensity or turnover time in the reactor, response time of the control system, and the ability of the chemical metering system to match process requirements.** If any one of these components is not properly designed, significant problems in system performance can be anticipated.

Methods used for pH adjustment are selected on the basis of overall cost because material costs vary widely as do equipment needs for different chemicals. The volume, kind, and quantity of acid or alkali to be neutralized or partially removed are also variables influencing the selection of a chemical agent (IWA, 2003)

2. FUNDAMENTALS OF CHEMICAL NEUTRALIZATION

2.1. pH

pH is the reference indicator for neutralization. Many chemical processes, such as metal precipitation and water softening, which are involved in neutralization, are pH dependent. pH is the negative logarithm of the H^+ ion activity in solution that, in waters where the ionic strength is not very high, can be replaced with molar concentration

$$pH = -log[H^+]$$

The process of neutralization is not only limited to bringing the pH to 7; it is invariably used in the processes, where pH adjustment to other than 7 is required depending on the chemical process in question. Some of the important chemical processes, where pH plays a significant role and where pH adjustment through neutralization is often required, are metal adsorption and biosorption, chemical precipitation, water softening coagulation and water oxidation (Goel, 2005).

2.2. Acidity and alkalinity

Alkalinity is the capacity of water to neutralize acids, whereas acidity is the capacity of water to neutralize bases. The amount of acid or base to be used in the neutralization process depends upon the respective amount of acidity and alkalinity (Goel, 2005).

2.3. Buffer capacity

The Word “buffer” stands for the stubbornness against any change. In environmental chemistry, buffers are always defined in the context of pH. PH buffers are those that resist any changes in solution pH when an acid or a base is added into the solution. They are very important in chemical neutralization processes. **Buffers generally contain a mixture of weak acid and their salts (conjugate base) or weak bases and their conjugate acid.**

In natural waters and wastewaters, if the buffering capacity of the flow to be neutralized is not taken into account, the actual amount of neutralizing chemical required may vary widely and causes operational problems.

2.4. Commonly used chemicals

The characteristics of most common chemical reactives used in neutralizing process are included on Annex 1.

3. DESIGN AND OPERATION

A proper engineering design should be based upon a variety of factors as optimum process parameters, laboratory scale tests and finally, cost analyses.

3.1. Neutralizing system selection criteria

Selection of **neutralizing agents** available should consider:

- Type and availability
- Reaction rate
- Sludge production and disposal
- Safety and ease of handling for addition and storage
- Total cost including chemical feed and feed and storage equipment
- Side reactions, including dissolved salts, scale formation, and heat produced
- The effect of overdosage

(Eckenfelder, 2000)

All neutralization process, irrespective of type of waste, share several basic features and operate on the principle of acid-base reaction. An adequate design of a neutralization process should consider the following:

- Influent wastewater parameters
- Type of neutralizing agent used
- Availability of land
- Laboratory scale experimental results

The overall design of neutralization process involves the design of the following features:

- Neutralization basin
- Neutralization agent requirements based on theoretical and treatability studies
- Neutralization agent storage (e.g. silo, silo side valve, dust collector, and foundation design)
- Neutralization agent feeding system
- Flash mixer design

The practical aspects like neutralizing agent close supplier availability, and therefore reduced transport costs, play an important role on the design process (Goel, 2005).

3.2. System design: batch or continuous

Neutralization can be carried out in either batch or continuous mode. In batch mode, the effluent is retained until its quality meets specifications before release. Several processes can be simultaneously carried out when the process is performed batchwise. Batch processes are good for small scale treatment plants or small waste volume. **For large volumes, a continuous neutralization process is typically used** (Goel, 2005).

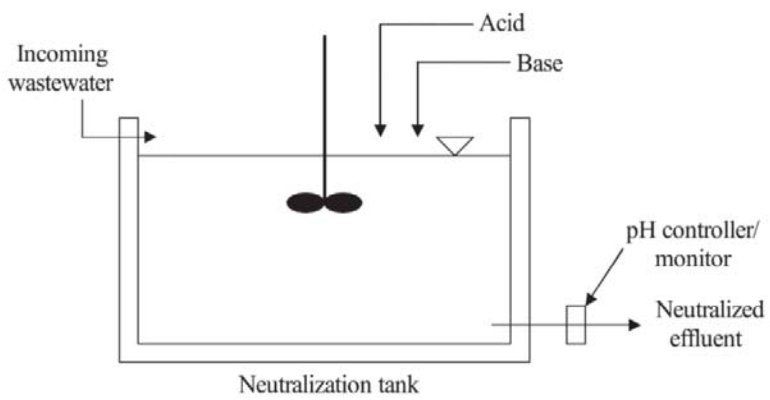

Figure 1.- Continuously operated neutralization tank (Goel, 2005).

In general, continuous flow-through systems are used when

- Influent flow is relatively constant and sudden variations are not expected
- The influent flow characteristics are essentially constant
- Effluent chemistry is not very critical. An example is when the process is a part of multi-stage neutralization process.
- Batch neutralization systems are used when:
- There are large fluctuations in influent properties (e.g., flow and pH).
- The influent wastewater contains concentrated acids or bases.
- The effluent quality has stringent discharge limits.

Batch treatment is used for waste flows to 380 m^3/d. Continuous treatment employs automated pH control. Where air is used for mixing, the minimum air rate is 0.3-0.9 m^3/min.m^2 at 2.7 m liquid depth. If mechanical mixers are used, 0.04-0.08 kW/m^3 is required (Eckenfelder, 2000).

The process is normally designed in order to reach a certain pH, however, in many cases it is enough to maintain the effluent pH within a range. This generates an error margin around the design objective pH.

3.3. Design parameters

On **Table 1** fundamental design parameters for a pH regulation process are summarized.

Table 1.- Design parameters on a neutralization system (modified from Eckenfelder, 2000).

Chemical storage tank	Liquid - use stored supply vessel Dry – dilute in a mix or day tank
Reaction tank: Size Retention time Influent Effluent	 Cubic or cylindrical with liquid depth equal to diameter 5 to 30 min (lime-30 min, the others less) Locate at tank top Locate at tank bottom
Agitator: Propeller type Axial-flow type Peripheral speeds	 Under 3.8 m^3 tanks Over 3.8 m^3 tanks Tanks less than 3.8 m^3: 0.76 m/s Tanks over 3.8 m^3: 0.36 m/s
pH sensor	Submersible preferred to flow-through type
Metering pump or control valve	Pump delivery range limited to 10 to 1; valves have greater ranges

4. PROCESS CONTROL

The automatic control of pH for wastestreams is one of the most troublesome, for the following reasons:

1. The relation between pH and concentration or reagent flow is highly nonlinear for strong acid-strong base neutralization, particularly when close to neutral (pH 7.0). The nature of the titration curve as shown in **Figure 3** favors multistaging in order to ensure close control of the pH.

2. The influent pH can vary at a rate as fast as 1 pH unit per minute.
3. The wastestream flow rates can double in a few minutes.
4. A relatively small amount of reagent must be thoroughly mixed with a large liquid volume in a short time interval.
5. Changes in buffer capacity (i.e., alkalinity or acidity) will change neutralization requirements.

(Eckenfelder, 2000)

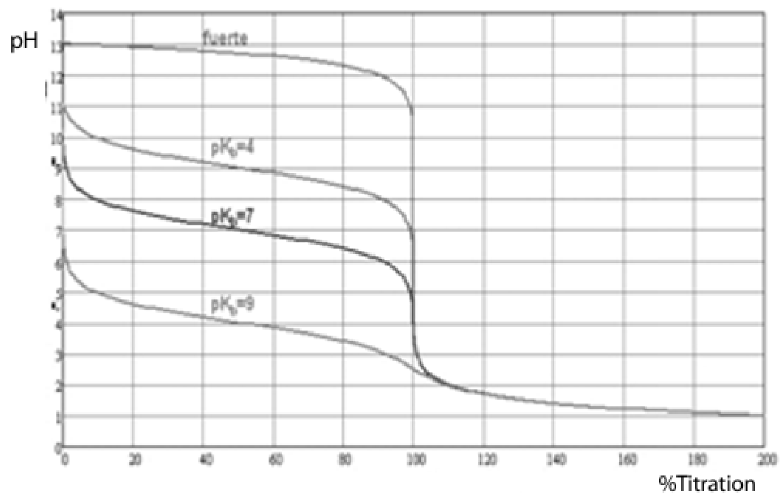

Figure 2.- Example of a titration curve for different basic solutions with a strong acid (Harris, 2007).

If affluent pH is normally **2 units above or under the objective pH level**, system is normally designed as a multistage process (Figure 4). In reaction tank 1, the pH may be raised to 3 to 4. Reaction tank 2 raises the pH to 5 to 6 (or any other desired endpoint). If the wastestream is subject to slugs or spills, a third reaction tank may be desirable to effect complete neutralization (Eckenfelder, 2000).

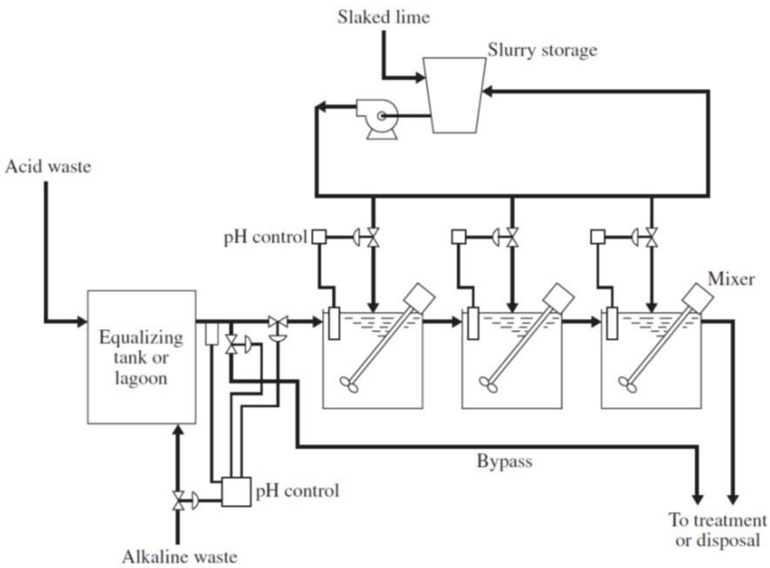

Figure 3.- Multistage neutralization process (Eckenfelder, 2000).

5. SPECIFICATIONS FOR TEXTILE INDUSTRY EFFLUENT TREATMENT

Most part of the process water and industrial effluent treatments requires a pH regulation as part of the treatment line. Some of the possibilities for pH regulation process locations on textile industry water lines are summarized below:

5.1. Process water pre-treatment

After water softening process (hardness removal), it is commonly required the pH regulation of alkaline streams. Besides, it will be required after metal precipitation processes (in basic media).

Metal adsorption and biosorption processes are especially dependent on pH values in the low range. If this process application is desired, acid water neutralization pre-treatment is recommended so as to maintain the pH level above 6.

5.2. Mill effluent pre-treatment

Generally, in the dyeing industry, effluents are highly alkaline and require the addition of acid. However, provision should be made to be able to add both acid and alkali, as some dyeing processes may give acid effluents and addition of alkali may be needed (Khan, 2006).

PH regulation processes use to be located in the homogenization tank of the ETP, along with its outlet. Table 2 shows alkalinity and pH ranges in the textile mills ETP inlet flows from different sources.

Table 2. Alkalinity and pH ranges in textile mill wastewater (Hussein, 2013; Paul, 2012; Babu, 2007; Fox, 1996).

Parameter	Minimum	Maximum
pH	1.8	12.6
Total alkalinity (mg $CaCO_3$/L)	17	800

5.3. On the ETP treatment line

PH regulation is useful inside effluent treatment plants with physical-chemical treatments. Since the addition of flocculants decrease alkalinity, lime uses to be dosed to prevent abnormal decrease in pH value, which may affect the flocculation and also helps to precipitate metal hydroxides in this treatment step. These processes normally require, after primary clarification, a pH neutralization step (Meenakshipriya, 2008).

In some cases, neutralization system is designed in order to elevate pH well enough to provide the necessary alkalinity to compensate the effect of a downstream process, like biological nitrification (Goel, 2005).

In secondary treatments, the biological system pH has to be generally maintained between 6.5 – 8.5 in order to assure an optimum biological activity. The process provides on its own certain neutralization and buffering capacity as a result of CO_2 production, which reacts with caustic and acid materials. The neutralization degree depends, therefore, on the DBO removal ratio and the acidity or alkalinity present on the wastewater (Eckenfelder, 2000).

6. CONTROL PARAMETERS AND STRATEGIES

The pH of the water after the equalization tank as well as water after coagulation, flocculation and biological treatment, and discharge water should be monitored regularly. For monitoring, a pH meter gives much more accurate result than pH paper, especially when the effluent is highly colored, and therefore pH paper should not be used.

An automatic pH controller should be used so that the pH can be automatically tested and adjusted. If an automatic pH controller system is not fitted samples must be taken regularly (at least every 2 hours) to ensure the efficient functioning of the ETP. Ideally the fitting of an automatic system should be considered as it will significantly improve the operation of the plant and will prove to be cost effective.

Spare pH meters and electrodes should be kept in stock to replace damaged electrodes without delay as pH control is crucial to the success of the ETP. The pH electrodes should be selected carefully and should be guaranteed by the manufacturer to be suitable for use in an industrial ETP since not all electrodes can withstand conditions in an ETP (Khan, 2006).

7. OPERATION AND MAINTENANCE TROUBLESHOOTING

Attention to security: Proper precautions must be taken to protect workers when handling NaOH, HCl or other chemicals used to correct the pH, as they are strongly corrosive and potentially dangerous. HCl is corrosive to concrete and steel so precautions need to be taken to ensure that the acid is not spilt onto the fabric of the ETP (Khan, 2006).

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ANNEX 1.- COMMON REACTIVES ON NEUTRALIZATION PROCESS CHARACTERISTICS (Eckenfelder, 2000)

Neutralization products characteristics summary

Property	Calcium carbonate ($CaCO_3$)	Calcium hydroxide ($Ca(OH)_2$)	Calcium oxide (CaO)	Hydrochloric acid (HCl)	Sodium carbonate (Na_2CO_3)	Sodium hydroxide (NaOH)	Sulfuric acid (H_2SO_4)
Available form	Powder, crushed (various sizes)	Powder, granules	Lump, pebble, ground	Liquid	Powder	Solid flake	Liquid
Shippingcontainer	Bags, barrel, bulk	Bags (50 lb), bulk	Bags (80lb), barrels, bulk	Barrels, drums, bulk	Bags (100 lb), bulk	Drum (735, 100, 450 lb)	Carboys, drums (825 lb), bulk
Bulk weight, lb/ft^3	Powder 48 to 71; crushed 70 a 100	25 a 50	40 a 70	27,9%, 0,53 lb/gal; 31,45%, 9.65 lb/gal	34 a 62	Varies	106, 114
Commercial strength	---	Normally 13% $Ca(OH)_2$	75 a 99%, normally 90% CaO	27.9%, 31.45%, 35.2%	99.2%	98%	60° Be, 77.7%, 66° Be, 93.2%,
Water solubility (lb/gal)	Nearly insoluble	Nearly insoluble	Nearly insoluble	Complete	0.58 32°F, 1.04 50°F, 1.79 68°F, 3.33 86°F	3.5 32°F, 4.3 50°F, 9.1 68°F, 9.2 86°F	Complete
Feeding form	Dry slurry used in fixed beds	Dry or slurry	Dry or slurry [must be slaked to $Ca(OH)_2$]	Liquid	Dry, liquid	Solution	Liquid
Feeding type	Volumetric pump	Volumetric metering pump	Dry-volumetric, wet slurry (centrifugal pump)	Metering pump	Volumetric feeder, metering pump	Metering pump	Metering pump
Accessory equipment	Slurry tank	Slurry tank	Slurry tank, slaker	Dilution tank	Dissolving tank	Solution tank	---
Suitable handling materials	Iron, steel	Iron, steel, plastic, rubber hose	Iron, steel, plastic, rubber hose	Hastelloy A, selected plastic and rubber types	Iron, steel	Iron, steel	---
Comments	---	---	Provide means for cleaning slurry transfer pipes	---	Can cake	Dissolving solid forms generate much heat	Provide for spill cleanup and neutralization

ANNEX 2
GRAPHICAL DESCRIPTION OF PROCESS UNITS

Figure 1. PH regulation system (Drinking water treatment plant -Lugo)

Figure 2. Head pH regulation chamber (Drinking water treatment plant-Lugo)

Figure 3. pH regulation system on a textile mil ETP (Zhejiang Lifeng. 100 m^3/h)

Figure 4. pH regulation addition system on a physical-chemical treatment ETP. (Arteixo. España)