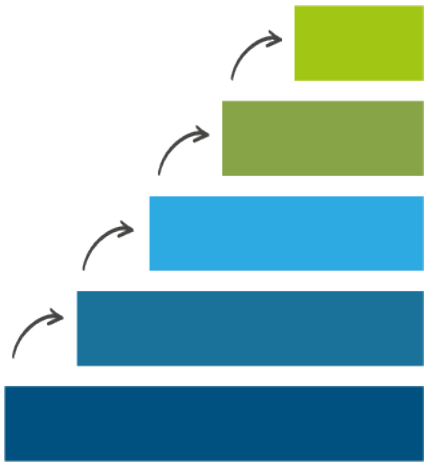
BALTIC INDUSTRIAL SYMBIOSIS

Generic case

RESIDUAL ACIDS AND BASES



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THE MAIN POINTS

Industrial symbiosis based on residual fractions that contain acidic or basic properties can create both economic and environmental benefits because reuse saves the procurement of new industrially produced chemicals and at the same time reduces the cost of disposal.

Residual fractions with acidic or basic properties come from collected acids/bases from different industrial processes or acids/bases contained in wastewater. Typically, residual acids and bases are waste products that must be disposed of via the sewer after neutralization or as hazardous waste. Both disposal methods pose a high cost for enterprises.

UTILIZATION

Residual acids and bases can be reused in processes where it is not problematic if the acid or base contains traces of other substances. It can, for example, be acids and bases from purification processes that place very high purity requirements but do not significantly pollute the substance or use up its strength.

For example, sulfuric acid can be used for slurry acidification, whereby lowering slurry pH reduces emissions of ammonia. Various acids and bases can also be reused for cleaning purposes and descaling of e.g. heat exchangers, cooling towers, and neutralization of basic cooling water.

Another utilization is neutralization of residual acid or base at another company. Mutual wastewater neutralization is a utilization with great potential, as wastewater flows from different companies can neutralize each other.

GREAT SAVINGS

Reuse of acids and bases ensures the utilization of their properties and therefore makes them a valuable resource rather than a waste product. By reusing acids and bases in industrial symbiosis, significant financial savings can be achieved. For example, in the form of reduced purchases of new acids and bases, payment to waste transporters as well as costs for disposal and waste handling if the acid/base is disposed of as hazardous waste.

Thus, symbiosis cooperation is advantageous for the bottom line because it strengthens competitiveness and at the same time is good for the environment.

ACIDS AND BASES

Acids and bases are applied in a wide range of industrial processes. Acids and bases can also be generated as by-products, whereby they are not directly involved in the company's processes. For example, fractions with acid or base properties occur in companies with the following processes:

- Surface treatment of metals
- Production of gases and chemicals
- Descaling heat exchangers, cooling towers etc.
- Washing/cleaning
- Neutralization

Residual acids and bases from companies can either be collected separately or mixed with the company's wastewater, thereby making it acidic or basic. In this case, the notion of acids/bases includes all residual fractions with acidic or basic properties and thus consists of generated acids and bases, wastewater and the like. It is generally the case that there are most utilization possibilities for separated fractions, rather than, e.g. wastewater that typically contains several different fractions.

Residues with acidic or basic properties are widely regarded as waste products for the companies and thus pose a disposal cost to the holders of these waste products. Acidic or basic wastewater is often neutralized before it is discharged into public sewers to avoid corrosion of sewage pipes.

However, many companies use acids/bases, and therefore there are many potential customers. The utilization of acids/bases depends on what kind of acid or base it is and in what concentration and what substances it contains. Strong acids and bases in high concentrations react more readily with their surroundings increasing the risk of corrosion of equipment and the like.

In Denmark, acids and bases are usually regarded as hazardous waste and hazardous freight[1], which, according to "The Order on Road Transport of Dangerous Goods"[2] and "The Waste Order"[3] must be collected and disposed of by an approved waste carrier, which is also costly.

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[1] Hazardous waste is defined in Appendix 4 of "The Waste Order", hazardous goods are defined in "The Order on Road Transport of Dangerous Goods", Appendix A.
[1] Order No. 788, dated 27/06/2013
[1] Order No. 1309, dated 18/12/2012

UTILIZATION

In most cases, neutralization is the only way to dispose of acids and bases either at the company or a waste treatment plant. However, it is possible to reuse acids/bases in production or for the neutralization process instead of newly purchased chemicals.

In the following, various utilizations of acids and bases are reviewed. Firstly, the possibilities that typically impose the strictest requirements on the type and properties of the substances are presented. In order to achieve the highest economic gain, reuse of acids/bases is the most optimal, which can be illustrated as a pyramid. An increase in level represents an improved utilization of the residual's properties and thus, a greater economic and environmental value. Therefore, the highest value is achieved by using high purity acids/bases for purposes that require it, rather than for purposes where the type of acid/base and their purity is not nearly as significant.

INDUSTRIAL PROCESSES

Acids can be used for a wide variety of industrial purposes, especially in surface treatment of metals. For example:

- Staining of stainless steel (nitric and hydrofluoric acid)
- Passivation (nitric acid)
- Electric polishing (sulfuric and phosphoric acid)
- Decontamination ("semi-weak acids", e.g. phosphoric acid, citric acid, formic acid etc.)

For cleaning processes, both acids and bases can be used (especially hydrochloric acid and sodium hydroxide/lye).

For some of these industrial processes, acid or base from other operations can be used if the process permits, e.g. traces of metals or other contaminants.

ACIDIFICATION OF SLURRY

In Denmark, more than 10% of slurry in stables is acidified to reduce ammonia evaporation, and this tendency is increasing. For this purpose, only sulfuric acid can be used. The concentration can be down to 30%, which means that residues can potentially be suitable for this process. Their addition must not cause the exceedance of limit values for the specific substances covered by "The Danish Sludge Order" [1], as the slurry is subsequently intended to be spread on agricultural land.

NEUTRALIZATION OF WASTEWATER

Typically, industrial wastewater should be within the pH range of 6.5-9 when discharged into the public sewer system to avoid corrosion of sewage pipes. If the water has a pH that is too low or too high, it must be neutralized at the company. For neutralization, purchased industrially produced acids or bases are typically applied.

However, residual acids and bases can be suitable for this purpose, as there generally are no high requirements for the purity of a neutralizer.

BUFFER CAPACITY

The buffer capacity of a solution is the solution's ability to neutralize acid/base without significantly changing the pH.

Softened water typically has a low buffer capacity. It causes large pH fluctuations and makes neutralization difficult.

Municipal wastewater, on the other hand, has a larger buffer capacity. Therefore, municipal wastewater can, in some cases, neutralize process water as effectively as industrially produced acids and bases.

Municipal wastewater can also be used for neutralization, although it has close to a neutral pH, due to the buffer capacity of the water, which is described in the information box.

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[1] Order No. 1650, dated 13/12/2006

[2] Order No. 9810, dated 31/05/2006

Therefore, companies with the need for neutralization should consider establishing mutual neutralization in collaboration with utilities. Thus, acidic or basic wastewater flows from different companies can neutralize each other with the possibility of adding municipal wastewater. It reduces or potentially eliminates the need to add industrially produced chemicals.

Several wastewater treatment plants in Denmark receive either acidic or basic wastewater for neutralization. Since the neutralization takes place before the purification process which the added acid/base undergoes, many acids/bases are suitable for neutralization at wastewater treatment plants. Therefore, it may be advantageous for a given company to allocate residual acids or bases to wastewater treatment plants, thereby replacing industrially produced substances.

DESCALING

In heat exchangers and cooling towers, limescale forms impairing heat transfer and thus energy efficiency. The limescale also shortens their service life. Therefore, the equipment is regularly decalcified with various acids.

Descaling is an example of a possible utilization with no high requirements for the purity of the acid and therefore, it is suitable for this purpose.

NEUTRALIZATION OF COOLANT

In large water-cooling plants, for example, in the pharmaceutical industry, a natural increase in pH must be controlled with acid. A wide range of acids can be used for this purpose if they do not contain substances that can damage the cooling system. In aluminum-based water systems for energy purposes, there is also a natural pH increase in reactions with aluminum ions from the pipes. Again, most acids will be useful for pH regulation in such systems.

EXAMPLE - MUTUAL NEUTRALIZATION

Two neighboring companies produce large quantities of basic and acidic process water in connection with their respective productions. To meet the discharge requirements, the companies neutralize the water locally in separate neutralization basins using industrially produced acids and bases. In collaboration with the municipal utility, the two companies can establish a mutual neutralization tank. By mixing process wastewater from both companies, the water will move towards more neutral conditions reducing the overall need for additives. It may also be possible to add municipal wastewater. This stream of water has a considerable buffer capacity, which can be exploited and thus, will further reduce or eliminate the need for adding chemicals

ECONOMIC PROFIT

The financial gain depends on how the acid or base has been disposed of as a starting point. A considerable amount of chemicals is disposed of as hazardous waste, with costs up to EUR 147/ ton. The high disposal costs make it economically viable to send residuals of acid/base to another company.

Common to all the reviewed utilizations is that there is a reduced need for procurement of industrially manufactured chemicals. If acid/base is supplied to another company rather than disposed of as hazardous waste, the recipient company saves the purchase of new chemicals. For example, if a company uses 11 m3 of hydrochloric acid (HCl) per year to descale its process equipment and can receive residual acid for this purpose free of charge, an economic saving of around EUR 2,946 per year is obtained. The supplier of the residual acid can obtain a corresponding saving if the substance is previously neutralized with base.

If residual acids are used for descaling, the companies can potentially descale more often as the cost of the acid is reduced or completely free. Descaling results in more energy-efficient operation and extends, among other things, the life of the heat exchanger. In this way, operating costs can be reduced.

Acid/base symbioses are particularly advantageous, as both companies achieve savings in connection with the purchase of chemicals and reduced operating costs.

In the mentioned symbiosis, the two companies have significant costs of process water neutralization, which they perform separately. By neutralizing jointly, the municipal utilities can offer this service at an advantageous price, compared to the cost of separate neutralization.

ENVIRONMENTAL VALUE

The reuse of acids/bases displaces the use of industrially produced acids/bases. It is very different how acids and bases are manufactured. Still, the process is typically energy-intensive and requires raw materials to be extracted from the soil with consequent environmental impacts. For example, sulfuric acid is derived from elemental sulfur and pyrite to be excavated from mines, while sodium hydroxide is produced by electrolysis, which is a very energy-intensive process.

The displacement of virgin acids/bases through symbiosis reduces consumption of limited resources. The environmental and health challenges of mining are also overcome. In addition, energy consumption and thus, its environmental impact are also reduced.

If a company applies residual acid/base for neutralization, industrially produced substances can potentially be displaced entirely. In other uses, there will probably be a reduction in consumption of acids or bases, which is, however, still of considerable environmental value.

The reuse of acids/bases has a double environmental benefit as both the supplier and the recipient avoid using industrial acids/bases for neutralization and other purposes.

In cases where residual acids are used for descaling, environmental savings can potentially be achieved. If increased decalcification becomes economically advantageous due to cheaper acid, a company can repeat this procedure more often reducing the consumption of process energy.

The environmental benefits of the mentioned symbiosis are reduced energy and resource consumption in connection with the production and transportation of industrially produced acids and bases.

BARRIERS

There is a variety of technical and/or regulatory barriers that can make it difficult to establish a symbiosis in which acids or bases are utilized.

PURITY OF THE FRACTION

When reusing residual acids/bases, the presence of impurities in them may not affect the process in which they are applied.
Typically, acids/bases cannot be used for production if it is not entirely pure. However, the application range of acids/bases means that most acids/bases can be utilized where the contaminants are not a problem.

Content of heavy metals can generally be a barrier. When acids/bases are used for wastewater treatment, the additional heavy metals must not affect the heavy metals contained in sludge to such an extent that the sludge cannot comply with the limit values according to “The Danish Sludge Order”.

For other applications, there are often higher requirements for the type or strength of the acid/base. Thus, to establish a symbiosis with acid/base, the right acid/base types must be matched with the proper means of application so that the full potential of the residual can be exploited without creating complications.

HANDLING ACIDS AND BASES

Acids and bases have corrosive properties, and some of them are also toxic. Therefore, there are several safety measures in connection with their transportation and handling. Acids/bases are generally categorized as both hazardous waste and hazardous freight, which stipulates a number of requirements on transport and use.

In Denmark, toxic acids and bases, e.g. hydrofluoric acid, also require a poison certificate before a company can handle it.

A logistics operator typically already has the necessary permits and skills to handle various acids and bases.

Therefore, it is expected that a certain amount of acid/base is required before the costs of complying with these requirements can be managed while still generating a profit.

This case reviews symbiosis possibilities for acids and bases and aims to inspire better utilization of this residual by describing options and benefits of such symbiosis. Please, do not use the case as a design or decision basis.

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