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LIME IN ENVIRONMENTAL USES
INDUSTRIAL WASTE TREATMENT WITH LIME

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In the late 1970's the US Environmental Protection Agency issued the Superfund law, the Resource Conservation Recovery Act (RCRA), and the Toxic Substance Control Act (TOSCA), which set the stage for reducing emissions of toxic waste products from industry and forced us to review our manufacturing processes toward the recovery of basic materials, and the safe disposal of non-recoverable waste materials.

The law specifies that reductions of emissions from plants must be accomplished to specific levels and that waste products must be disposed of in a secure licensed landfill. These landfills must be secure, in that they must not allow leachate to leak into the surrounding groundwater and contaminate aquifers. The site must be geologically stable and above the flood plain. Monitoring wells must be installed and continually monitored for leachate contamination.

Lime, calcium hydroxide, is used to render many of the wastes safe for disposal and also can be used to form an impermeable layer in the secure landfills, to prevent leachate contamination of the groundwater. Lime is also used to treat leachate collected from run-off from these landfills.

Liquid Wastes

In the treatment of aqueous solutions containing heavy metals such as lead, cadmium, zinc, copper, arsenic, etc, lime is used to adjust the pH of these solutions to precipitate insoluble hydroxides and calcium complexes of these contaminants. After filtration, the waters are safe for disposal and the sludges are chemically fixed, safe for disposal and are non-leachable.

Acid wastes such as pickling liquors and other waste acid streams are neutralized with lime to form insoluble, safe compounds like gypsum sludges. Low pH water streams are neutralized with lime, prior to safe discharge into receiving streams.

Corrosive Waste

The hazardous waste laws define a corrosive waste as a liquid with a pH of 2 or less, or a pH of 12.5 or greater. Lime wastes are specifically excluded from the hazardous waste laws. However, if any waste exhibits the corrosive characteristics, ie, liquid, pH 2 or less or 12.5 or greater, then it is a corrosive hazardous waste, and must be treated as such.

Lime in a saturated solution has a pH of 12.454 at 25°C. This was the basis of defining hazardous as 12.5 or greater.

pH

As you know, the pH scale of 0 - 14 is based on the fact that water has equal concentrations of Hydrogen ions (H^+) and Hydroxyl ions (OH^-) at 25°C, giving water a neutral position of pH 7. This is only true at 25°C! This temperature relationship is not too important at neutral or medium pH ranges. However, at pH's approaching the regulatory limit of 12.5, the temperature relationship becomes very important, especially when measuring pH's of lime based solutions. The soluablity of lime is inverse to the temperature. So you see, if one measures the pH of a lime solution at temperatures below 25°C then the pH reading will be incorrect and read high, possibly above 12.5, falsely suggesting the solution is hazardous! This, of course is not true! Temperature must be taken into consideration when reading pH levels approaching this regulatory level!

A higher temperature is also misleading. Suppose one measures the pH of a hot lime treated mixture, and one attempts to add sufficient lime to reach a pH of 12 or greater. If the temperature is above 25°C the pH reading will be incorrect and read too low. If the temperature approaches 100°C, one probably cannot attain a pH of 12 even though excess lime is used, probably only 11 or 11.5! pH samples should be temperature adjusted to 25°C prior to reading in order to be accurate. Again, temperature must be taken into account when reading pH.

Solid Waste

Industrial sludges/wastes that are hazardous due to toxic contaminants, especially heavy metals are also mixed with lime to form insoluble compounds, which are non-leachable. Often these sludges can be de-listed, ie: classified as non-hazardous and disposed or reused without further regulation.

In treating hazardous wastes we often use lime, portland cement, fly ash, lime kiln dust, cement kiln dust or a mixture of these materials. We highly recommend that each waste be evaluated in the laboratory, first neutralized with sufficient lime and then solidified with mixtures that form pozzolonic compounds. Pozzolonic compounds are mixtures of lime and materials like fly ash when mixed together make a cement. This gives structure and strength to the treated material so it can be used as an engineering fill material or as a raw material for block making.

Oily Waste

Oily waste can successfully be treated with lime to form insoluble calcium soaps which are non leaching, this is a non-reversible reaction called saponification (soap making). However, there are pit falls one must be aware of and avoid to have a successful conclusion.

The addition of dry lime to an oily waste will simply soak up the water and oil but not react to form insoluble soaps. If one takes this dry treated material and compresses it, liquid will be squeezed out of the mixture. This is not a stabilized mixture.

To properly treat oily wastes, a lime slurry is used - and preferred temperatures of around 50° - 70°C. At these temperatures the saponification reaction occurs quite rapidly forming calcium stearate - calcium soap. The saponification reaction is not reversible. If a structural material is desired, then sand or soil is mixed with the soap to give it structure.

Pozzolonic materials can also be mixed with the soap/sand mixture to form a cement like material with considerable strength.

Refuse Derived Fuel

Combustible organic wastes like saw dust, vegetable wastes, hulls, paper etc can be mixed with lime and pelletized into Refuse Derived Fuel pellets. In this form the fuel can be stored for long periods then used as fuel, as a replacement for coal, etc. I'll talk more about RDF when we discuss municipal solid waste.

Chlorinated Hydrocarbons
(PCBs, Dioxins, Pesticides, Herbicides, Nerve Gas)

For years the EPA has listed the use of lime and lime containing materials as an acceptable way of solidifying and stabilizing PCB containing wastes. These materials are to be incinerated at a later date at 1500/2000°C.

About two years ago, some of these treated wastes were tested and no PCB could be found. Thus, begins the great debate "What happened to the PCB's"? EPA let a contract with a midwest laboratory in an effort to simulate what was happening in the field. The researcher did not expect to destroy PCBs with calcium oxide, but did set up simulated field trials. To his surprise, he did find PCB destruction! He believes that lime reacts with the chlorine radical and forms calcium chloride and other safe compounds. He has applied for a patent on his process.

EPA was not convinced and did some follow-up work in their lab at Cincinnati, Ohio. They could not duplicate the outside labs work and feels that volatilization and loss of the PCB is most likely what is going on. However, they suggest additional research needs to be done.

Previous to these findings, Dr. Bolsing of Hanover, Germany claimed to be able to destroy PCBs with lime. His experiments include passing PCBs in the gaseous phase through a calcium hydroxide bed at about 350° - 400°C. In this experiment, he shows about 80% destruction. Dr. Bolsing and Sound Environmental Services of Carlsbad, California claim they can achieve destruction at near ambient temperatures with additional proprietary chemical additives. Full scale trials are now being conducted.

As I mentioned in the RDF paper, at the Argonne National Laboratories trial burn of RDF with lime binder, there were no traces of PCBs/Dioxins, etc in the flue gases. I think this supports Bolsing's work that something is happening to the PCBs with lime.

At EPA's Research Triangle Park in North Carolina, Dr. Brian Gullette is studying emissions from waste incinerators and trying how to best control the toxic gases. He, too has experimented with passing dioxins and PCBs in the gaseous phase through a bed of calcium hydroxide at 350°C - 400°C, showing almost complete destruction. We understand his work has been peer reviewed and approved, but not published. Additional Department of Energy research funds have been approved for further research.

In Kansas, Dr. Kenneth Klabunde has published research on the destruction of PCB's with C_aO/M_gO calcium oxide and magnesium oxide. He makes extremely fine oxide particles by a special hydration process and then by recalcining the hydrate.

On passing the gaseous phase of PCB's and other chlorinated hydrocarbons through the reaction bed of C_aO/M_gO at temperatures of around 350°C - 400°C he sees complete destruction. His paper describes the chemical balances, by products and non-toxic end products, mainly calcium chloride.

As a result of further work with mimics of nerve gas, where he shows similar positive results, the Department of Defense has awarded him a $5,000,000 contract for further nerve gas destruction research.

Dr. Klabunde advised us that his basic research on Calcium Oxide and Magnesium Oxide led him to conclude that these Alkaline Earth Oxides are unique in the periodic table. They have unique properties as to heat of formation that makes them suitable for these special reactions. I, of course, hope he will find new break-throughs in the use of lime.

Of the many, many known uses of lime, we are still discovering how unique and versatile this material is.

Summary

Lime's use in industrial waste treatment is unique. Other alkaline materials are also used, but lime is unique in that the salts of the lime reactions are almost always insoluble. Alkaline salts such as caustic are almost always soluble.

As the objective of treating waters is to remove dissolved solids and leave a clean, pure water, it makes sense that lime is the obvious choice. It's true that lime treatment of waste waters generate more sludges, but isn't that exactly what we want to do?

Yes, remove the dissolved solids from the water, chemically fixing the sludge, so it is safe in the environment and leaving a safe, pure resource, pure water!

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