

CAUSTIC MAGNESIA IN ENVIRONMENTAL APPLICATIONS

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ABSTRACT

Caustic magnesia (MgO) and its derivatives are used in environmental control technology and compared to most commonly used alkalis (CaO, Ca(OH)₂, NaOH, NaHCO₃ etc) they present essential advantages. Their lower molecular weights result to the use of less quantities for pollutants neutralization or capture and therefore to the production of less waste quantities to be disposed. Their milder basic character makes them more environmentally friendly and they are classified as non-dangerous basic reagents concerning the safety for their transportation and use.

INTRODUCTION – GENERAL INFORMATION

Magnesia (MgO) is the product of the thermal decomposition of, mainly, magnesite (MgCO₃), following the reaction:



In aquatic environment magnesia transforms into the corresponding hydroxide Mg(OH)₂ which has low dissolution ability (1,5·10⁻⁴moles/lit(18°C)) and consequently a low dissolution constant (K_{sp}=1,3·10⁻¹¹(18°C)) which determine the pH of the solution in relatively milder values. Theoretically, the pH of a saturated solution-slurry is about 10.5, but in reality, given the presence of other ions or even magnesia syndromes, buffer solutions are formed with pH = 9-9,5.

Because of its basic character it is used in various environmental applications ^[1] and its role is multiple. The most important applications as well as the benefits of using magnesia instead of other traditionally used reagents are mentioned below:

1. NEUTRALIZATION OF ACID WASTEWATER



- The stoichiometrically demanded quantity of MgO for the neutralization of a certain amount of acid wastewater is significantly lesser than the quantities of other basic agents like Ca(OH)₂, NaOH, Na₂CO₃ etc.

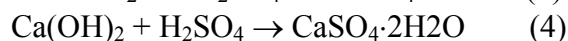
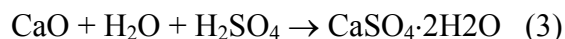
Another important advantage of MgO is the smaller quantities of the possibly resulting solid waste, which has an important disposal cost.

- Caustic magnesia is, compared to other reagents, a milder basic agent. Even in cases of overdosing the pH of the wastewater will not raise above the legislation-set values for environmental disposal, due to the creation of a buffer solution.

On the contrary, using $\text{Ca}(\text{OH})_2$ or NaOH the pH may reach values of 12 or 14 correspondingly. Additionally, in these high pH values a non-reverse precipitation of carbonates' salts is observed which results to an increased volume of sludge, deposits in tank linings, pipes' obstructions etc. Finally, in

case that a biological procedure should be followed, it must be mentioned that, in such high pH values, the action of micro-organisms that biodegrade the organic load is inhibited. In case that the above mentioned strong basic reagents are used simultaneously for pH control and biological processing, the action of the micro-organisms is inhibited due the great variation of pH at the moment of the introduction of the reagents, while the introduction of a magnesium reagent exhibits a smooth pH variation with no consequent problems [2].

- The use of CaO or $\text{Ca}(\text{OH})_2$ for the neutralization of free H_2SO_4 (sulfuric acid) leads to the formation of gypsum which is responsible for many scaling and obstruction problems.



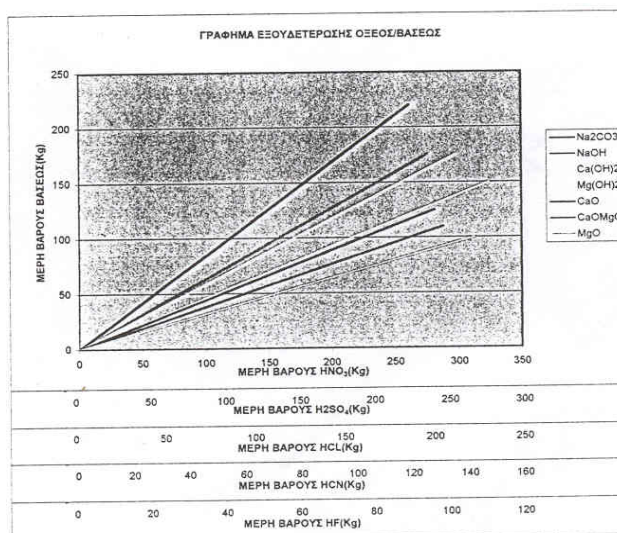
- NaOH solutions and $\text{Ca}(\text{OH})_2$ slurry are very corrosive for the installation and inflict dermatological irritations to the handling personnel, so they must be handled with special caution from the personnel that is responsible for the process. On the other hand, $\text{OH})_2$ slurry is not corrosive or dangerous to use.

- In case of water reuse for irrigation the presence of sodium salts make it unsuitable for this use, since the sodium ions de-agglomerate the soil and make it hard and impermeable to water (practically infertile).

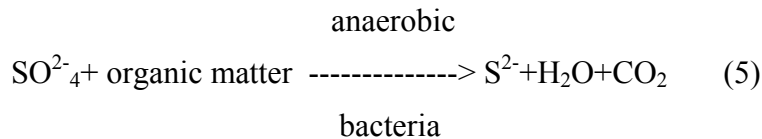
2. WASTE-WATER TREATMENT

The role of magnesia in waste-water treatment is multiple: odor control, protection of the sewerage network and the collection tanks, pH monitoring for stable conditions creation very important for the stage of the biological process, removal of the phosphates and ammonia etc.

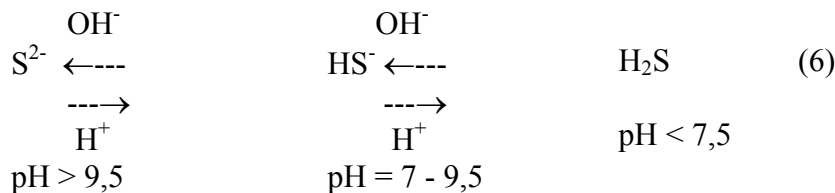
Odor control:



The problem of odors of wastewater in sewerage network is mainly attributed to H₂S evolution and less often to ammonia (depending on the pH of the wastewater)^[3]. The main source of H₂S is the reduction of sulfates by anaerobic bacteria following the reactions:



The presence of MgO provides the system with a buffer solution at 9-9,5, which based on reaction (6) prohibits the formation of H₂S, which is a main odour-creation factor. Independently of the S²⁻ concentration from the moment the pH is set at 9-9,5 the odor problem due to H₂S ceases to exist. Also at these pH values, no ammonia (NH₃) evolution is performed.



Other reagents used for this application are Ca(OH)₂, NaOH and FeSO₄. The first two as alkalis have the same operation principle as magnesia but strict control of the pH of the wastewater and a very good dosing system for the reagents is needed, in order to avoid sudden raise of the pH phenomena with undesirable results (increased sludge quantity due to carbonates' precipitation, obstructions, odor problems due to ammonia evolution etc.). Odor elimination using FeSO₄ is based on the following reaction:



Based on the above reaction, our observations include bonding of H₂S with the simultaneous formation of the corrosive H₂SO₄ thus demanding the additional treatment of neutralization. In other words, the use of FeSO₄ does not prevent the formation of H₂S but can be used effectively for its neutralization, although in this case the use of a mild basic reagent like MgO or Mg(OH)₂ is necessary for the neutralization of the forming H₂SO₄ and pH adjustment.

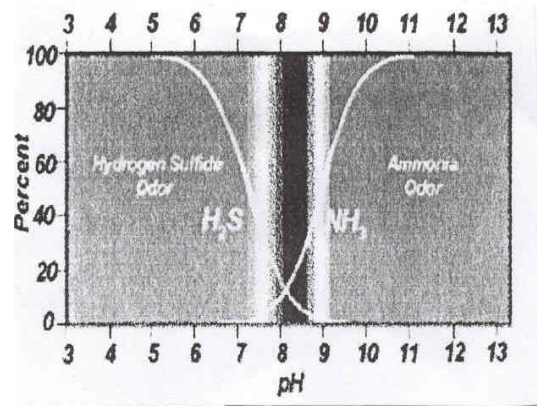
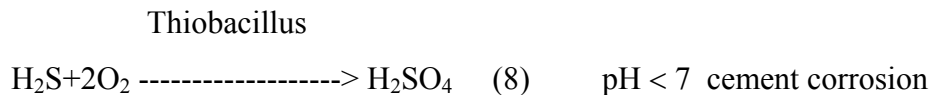


Figure 1: H₂S and NH₃ solubility vs. pH

2.2 PROTECTION OF THE SEWERAGE NETWORK AND COLLECTION TANKS

The corrosion of the sewerage network and tanks is attributed to the formation of H_2SO_4 through reaction (8):

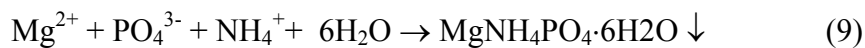


The protection of cement with the aid of basic magnesium reagents is performed through mechanisms: on one hand, they provide the system with OH^- groups which neutralize the H^+ groups and on the other hand they prevent the formation of H_2SO_4 since in values of $\text{pH} < 9-9,5$ the ionised form of H_2S exists (reaction 6). So the protection may be performed in two ways: either with continuous addition of $\text{MgO}/\text{Mg}(\text{OH})_2$ in parts of the network for pH adjustment or through coating the free surface of the pipes with $\text{Mg}(\text{OH})_2$ slurry.

2.3 REMOVAL OF PO_4^{3-} AND NH_4^+

The removal of PO_4^{3-} is of major interest lately since phosphates interfere with the phenomenon of eutrophism and lead to the mortification of aquatic life. In addition to the above due to decrease in natural phosphate deposits the recovery and recycling of phosphorous is imposed.

The reaction of phosphate and ammonia removal has been studied widely ^[4,5] and is described from the following reaction:



The product of reaction is called struvite and its formation depends on the pH of the system, the optimum value being $\cong 9,5$. Struvite crystallization is performed in fluidized-bed reactor (Crystalactor®). An important number of reactors (of semi-industrial or industrial scale) are in operation around the world.

Struvite can be used as a fertilizer (Mg,N,P source). Magnesium ions provoke the increase of the chlorophyll production since they occupy the central position in its molecule, while N and P are important nutrients for the plants. In such a case, there is also an economical advantage gained by its production from selling the fertilizer.

The use of $\text{MgO}/\text{Mg}(\text{OH})_2$ achieves the best possible recovery yield of the phosphates in comparison to $\text{Ca}(\text{OH})_2/\text{CaO}$ due to the more effective pH control ^[7].

3. HEAVY METAL REMOVAL IN INDUSTRIAL WASTES

From an environmental point of view heavy metals (Pb, Cu, Cd, Cr, Ni, Hg, Ag, An, Pt) present a great interest because:

- 1) They are expensive due to their rareness and when possible they should be recovered.
- 2) Are very toxic and for this reason maximum level concentration limits have been specified.

Several heavy metals dissolved in acid waste waters can be removed effectively as insoluble hydroxides, using caustic magnesia or $Mg(OH)_2$. The resulting sludge precipitates faster, requires less filtration time and is more compact in comparison to the one produced using other basic agents like $Ca(OH)_2$ and $NaOH$.

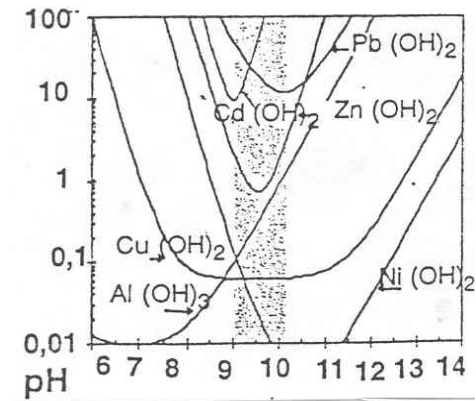


Fig. 2: Heavy metals' solubility

This difference is due to the fact that the precipitation, using MgO , has a controlled speed whereas with other basic agents the precipitation occurs with great speed resulting in the formation of microcrystalline material (time-consuming precipitation and filtration, high humidity content).

This difference is translated in significantly lower amounts of sludge for transport and disposal, with a corresponding cost benefit [9]. In addition to the above, in case of over-dosing of MgO , the pH does not exceed the maximum allowed values for wastewater disposal, unlike $Ca(OH)_2$ or $NaOH$ where pH may climb up to 12 or 14 correspondingly (environmentally unacceptable values).

Finally, we must add that most heavy metals hydroxides re-dissolve in high pH values, thus concluding in an insufficient removal from the waste and, in consequence, incompliance to the maximum concentration levels for waste disposal.

The tanning industry is a characteristic example of both heavy metal removal through precipitation and recycling, using MgO . The following reactions and Fig.3 illustrates the procedure:

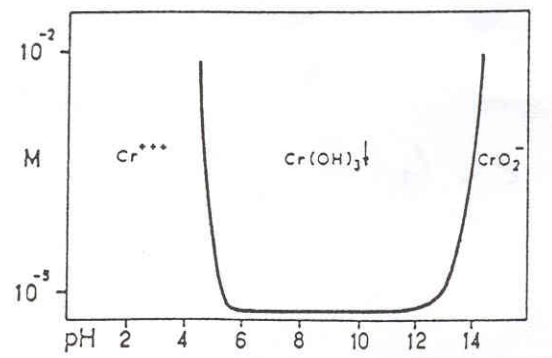
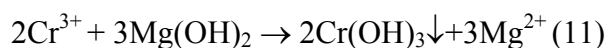
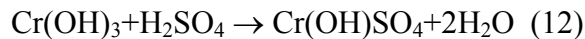


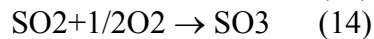
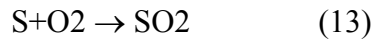
Figure 3: Cr^{3+} solubility vs. pH





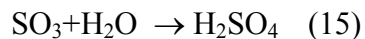
4. FLUE GAS TREATMENT IN ENERGY PLANTS

Energy plants use fuel oil which has a high sulfur (S) content, sometimes exceeding 3% of the fuel or other fuels with equally high S content. Sulfur at high temperatures reacts with oxygen following the reactions:



The percentage of the formed SO_3 depends on oxygen content (Fig....), the presence of elements that act as catalysts to the reaction (14) as well as other combustion parameters. The action and effects of SO_2 in the environment as well as in the functional availability of the installation are multiple.

When the temperature of the flue gas equals the condensation temperature of H_2SO_4 vapors ($\cong 130^\circ\text{C}$), SO_3 reacts with water vapors of the flue gas and forms sulfuric acid, which is very corrosive for the installation:



H_2SO_4 besides its corrosive properties can also form a kind of colloidal film when in contact with the cold parts of the installation's surface where new particles come to stick forming in this manner very hard and thick deposits. These deposits lower the efficiency of the heat-exchangers and reduce the inner diameter of the pipes that carry off the flue gases.

In addition to the above, if SO_3 escapes to the atmosphere it either form acid smuts, using the dust in the air, which cause corrosion in the immediate environment of the energy plant and are responsible for various types of respiratory problems in humans, or is the main cause for the formation of acid-rain phenomenon with destructive effects on the fauna and flora as well as on marbles, buildings and other constructions.

The role of MgO addition to energy plants is multiple:

It forms chemical bonds with sulfur oxides as well as other fuel syndromes like V, Na, K which create low melting point compounds and cause severe problems inside the combustion chamber and in the burners. In the first case, MgO is added previously to the air preheating exchangers, whereas in the second case it is added directly to the combustion chamber as Fuel Oil Additive where MgO leads to the formation of high melting point compounds avoiding thus scaling.

MgO also has stoichiometrical advantages, in comparison to other used reagents, as can be seen in the following table, where the stoichiometrical amounts of reagents for the neutralization of 1kg of SO_3 as well as the stoichiometrical amounts of the resulting products are given:

TABLE 1. Stoichiometric neutralization of 1kgr SO₃

Reagent		Reaction's product		
Reagent	Compound	Quantity (kg)	Compound	Quantity (kg)
1	MgO	0,504	MgSO ₄	1,504
2	CaO	0,700	CaSO ₄	1,700
3	Na ₂ CO ₃	1,325	Na ₂ SO ₄	1,772
4	NaHCO ₃	2,100	Na ₂ SO ₄	1,772

The reaction product using CaO is gypsum which creates hard deposits, obstructions and other functional problems in the installation, while sodium (Na) based reagents have higher cost and the reaction products are difficult to handle.

5. SOLID WASTE AND CONTAMINATED SOIL STABILIZATION

This case refers to sludge deposit lands, areas with former mining activities or other solid wastes containing heavy metals.

The solubility of the heavy metals and their hydroxides in acidic environment or even in a slightly basic environment is important. As a consequence, in acidic environment or even with rain the heavy metals or their hydroxides contained in these soils can dissolve and escape to the environment with unpredictable consequences to the public health.

Mixing the above mentioned wastes, before deposition, with MgO/Mg(OH)₂ or with immediate addition to the contaminated soil may prevent the leaching of heavy metals in the environment.

The role of magnesia is double:

- it neutralizes the acid responsible for the metal dissolution, leaving heavy metals in an undissolved state.
- it buffers the pH at 9-9,5 and in this way the re-dissolution of certain metal hydroxides (Cr, Zn, etc.) is avoided, a phenomenon that is observed in higher values of pH. The use of alkalis like Ca(OH)₂ or NaOH is not indicative because the pH may reach values of 12 and 14 correspondingly.

Addition of MgO or Mg(OH)₂ can also be made for the treatment of contaminated soils. In this case, after the soil has been removed (digging) it is mixed with the adequate MgO quantity, so as to create conditions that do not allow the leaching of heavy metals and then it is deposited in special landfills.

CONCLUSIONS

Caustic calcined magnesia is a very important reagent in the environmental technology and its position is expected to further strengthen, since the international policies for maximum contaminants limits tend to become stricter.

From a technical point of view and taking under consideration the total treatment costs, we may conclude that caustic magnesia excels the other reagents in many applications.