

Emerging Zeolite Technologies for Environmental Remediation

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Abstract

Understanding the interaction between zeolites and ions or molecules with which they come in contact presents us with increasing opportunities for the application of our new knowledge. Research at C₂C Zeolite Corp. for many years has focused on an understanding of the basic physio-chemical processes occurring with zeolites in the context of a variety of scientific disciplines. The knowledge gained allows us to exploit these unique minerals for a diverse set of situations. Current research emphasizes three environmental areas: immobilization and encapsulation of hazardous waste, remediation of contaminated soils and reducing impact of disposal. As the understanding of industrial minerals increases, new market opportunities present themselves. Our research into the characterization of natural zeolites has allowed us to remain at the forefront of new applications for this family of alumino-silicates.

Introduction

Zeolites are a group of naturally occurring alumino-silicate minerals characterized by their unique open framework molecular structure. The spatial distribution of silica and alumina tetrahedra in the lattice gives rise to a unique arrangement of pores, cavities and channels which are molecular in size. Furthermore, wherever an alumina group has substituted for a silica group in the crystal lattice, a net negative charge occurs which must be balanced by the positive charge of a cation. The honeycomb structure also results in a large and reactive surface area where the spatial arrangement of silica and alumina groups gives rise to charge imbalances at the surface. Again, the spacing between these charge differentials is molecular in size.

As a result, zeolites, which based on their composition would be generally regarded as non-toxic and inert, are in fact highly reactive at the molecular level as evidenced by their popular usage as catalysts and selective molecular absorbents.

The five characteristics of zeolites which are fundamental to an understanding of their functionality and their interaction with the environment are:

1. Zeolites have an open framework structure with pores, cavities and channels that are molecular in size. Small molecules pass through, large ones are excluded while intermediate ones are trapped. This molecular sieving capability allows selective separation, absorption and immobilization.
2. Wherever an alumina group substitutes for a silica group, a net negative charge exists. Cations bonded to these sites are exchangeable, affecting the equilibrium between ions in solution. Cation exchange capacities are typically 100 to 200 milliequivalents per 100 grams, much higher than typical soil.
3. The surface area of zeolite is in the 20 to 50 square meters per gram range. Furthermore, the charge differential between silica and alumina tetrahedra in the lattice results in a highly reactive surface. Absorptive processes are enhanced by bonding to these active sites.
4. The channels and cavities provide a large void volume for the minerals, allowing for retention of air, moisture and nutrients. Permeability and porosity is enhanced while also providing an ideal platform for microbiological activity.

5. Silica and alumina at the surface of zeolites are reactive. Zeolites are pozzolans and react in cementitious systems to enhance the strength, integrity and corrosion resistance of resulting concretes. The reactivity, the large surface area and the molecular porosity of the material all play a role in the stabilization of hazardous waste for encapsulation by zeolite concrete.

With an understanding of these characteristics of zeolite, C₂C has taken a multidisciplinary approach to developing technologies for the environment. Drawing on expertise in fields of environmental science, soil science, horticulture, concrete engineering and oilfield technology, three areas of environmental technology development have been pursued.

Waste Encapsulation

The US Environmental Protection Agency recognizes cementitious solidification as the “best demonstrated available technology” for land disposal of most toxic elements. Portland cement is commonly used in waste solidification because it is relatively inexpensive, highly alkali and can readily incorporate wet waste. While some reasonable success has been achieved, in many cases the waste is incompatible with the cementitious system.

The use of zeolites as a binding material prior to encapsulation capitalizes on the unique ability to absorb, trap and immobilize the contaminants in the zeolite structure. The contaminants are then no longer available to influence and interfere with the concrete development process. The zeolite fulfills two roles: Stabilizing the contaminants and contributing to the integrity and corrosion resistance of the resulting concrete.

Stabilization

- Volatile organic compounds are captured by molecular sieving
- Non-volatile organics are adsorbed onto the large surface area of the zeolite grains
- Heavy metals such as Pb, Cd, Zn, Ag, Hg are trapped by ion exchange
- Radioactive cations, Cs and Sr, are trapped by ion exchange
- Metals, including As, U, Cr, Mo may be immobilized by hydrogen bonding of oxyanions

Solidification

Encapsulating Zeolite Concrete is made with zeolite as a portion of the aggregate. It is manufactured with a situation-specific formulation, but using common, commercially available raw materials, cement and admixtures and normal, low-cost, energy efficient concrete manufacturing processes. The pozzolanic material traps and then quickly solidifies to physically envelop the hazardous waste into a strong, corrosion resistant concrete block or aggregate. Sufficient compressive strength (7-15Mpa) is achieved after curing for some load bearing situations. In many cases, a useful product will result. The encapsulated, stabilized product passes TCLP leachate tests and can be safely stored without fear of contaminants being remobilized, a permanent remediation.

Hydrocarbons

Zeolite with its capacity as a molecular sponge absorbs free hydrocarbons on contact from contaminated substrates. The longer the contact between contaminant and absorbent, the more the contaminant is absorbed. When we incorporate zeolites into invert drill cuttings, we find that the hydrocarbons are absorbed into the pores of the material due to the affinity that zeolite has for hydrocarbons. For heavier hydrocarbons, adsorption onto surfaces occurs. Zeolites have also demonstrated an unusual propensity for benzene, and other aromatics.

Hydrocarbons in Drill Cuttings: TCLP Leachate Test

	Untreated (ppm)	Encapsulated (ppm)
Total Hydrocarbons	105000	200.5
Benzene	282.8	33.3
Toluene	78.3	44.7
Ethyl Benzene	17.6	1.55
Xylene	69.0	16.0

Heavy Metals in Drill Cuttings

The disposal of drill cuttings from oil wells when invert drilling fluids have been used poses a problem because of high concentrations of hydrocarbons and heavy metals. The zeolite encapsulation process for these cuttings is approved as a disposal procedure.

Invert Drill Cuttings: TCLP Leachate Test

	Untreated (ppm)	Encapsulated Mud (ppm)
Cu	30.2	0.9
Co	11.8	0.2
Cd	0.5	<0.1
Ni	51.2	0.6
Pb	14.5	<0.1
Zn	112	0.1

Heavy Metals

Because of the anionic nature, zeolites have a natural affinity for a broad range of heavy metals, most notably lead, copper, zinc, mercury and chromium. It is found that once zeolite has formed an ionic bond with these metal contaminants that it is very difficult to sever this bond.

Lead Paint Residue: TCLP Leachate Test

	Pb(mg/L) in leachate	Pb(ppm) in solid
Untreated	1.03	103.3
Encapsulated	<.05	<1.0

Mine Tailings: TCLP Leachate Test

	Zn (mg/L)	Pb (mg/L)	Cu (mg/L)	Cd (mg/L)
Untreated	49.6	0.15	2.99	0.24
Encapsulated	0.08	0.04	0.01	0.005

Chemicals, Paint, Pesticides

Some of the more successful applications have been the stabilization of wastes such as lead paint and organic pesticides. Most hazardous waste facilities and controlled landfills are unable to take these contaminants in their liquid forms as it increases the possibility of penetration through their liner material. Use of zeolite to stabilize liquid contaminants followed by encapsulation allows disposal in landfill. This stabilization decreases the cost of disposal of this material dramatically. Latex paint waste can be turned into useful concrete products.

Pesticide Residue in Soils: TCLP Leachate test

	Unstabilized (ppm)	Stabilized (ppm)
2- ethyl 1- hexanol	6700	2400
2,4 -D, iso butyl ester	2340	1400
2,4 -D alkyl ester	6870	2800
2,4,5 -T iso butyl ester	530	190

Key to Encapsulation

The evolution and use of zeolite as a stabilizer prior to the formation of concrete is the key to the success of encapsulation. The ability of the material to absorb and strongly bond to contaminants reduces their availability to leaching or interfering with the development of strong concrete. The lab results indicate that there is a sharp reduction in the amount of leachable contaminant when zeolite is included in the concrete formulation.

The molecular sieve capability of zeolite continues to trap contaminants in concrete even when it is crushed, since the particle are still many times larger than the molecular chambers trapping the toxins.

Adaptation of the unique chemical properties of zeolites to concrete encapsulation was initiated by C₂C and contracted to the Institute for Research in Construction of the National Research Council of Canada (NRC). The investigation and research resulted in Canadian, U.S. and Mexican patents being issued for Encapsulating Zeolite Concrete. (US Patent # 5,494,513, Canadian Patent # 10476-2, Mexican Patent # 195989)

Soil Remediation

Fertile soils which have been subjected to harsh treatment by industry, contamination by chemicals, excessive destructive farming practices and sometimes through natural causes often have lost their ability to support healthy vegetation. Sustainable growth is possible only if adequate aeration, moisture retention and nutrient concentrations are present. Furthermore, the impact of any contaminants must be reduced to a non-toxic level.

The requirements for good, fertile soils are synonymous with the characteristics of zeolite:

- high ion exchange capacity
- high moisture retention
- high nutrient retention
- good aeration

In addition, zeolites are capable of absorbing and trapping toxic contaminants, buffering pH and moderating the equilibrium between alkali metals so that effect on vegetation is reduced. While they contain no inherent nutrient value, they are an excellent grow medium as evidenced by their use as hydroponic substrates. The large surface area provides an excellent platform for microbiological activity as evidenced by our research into composting and bioremediation.

Bioremediation

Composting of hydrocarbon contaminated soils can be accelerated by intimately incorporating 10 to 15% granular zeolite into the mix. Moisture, nutrients and oxygen levels are moderated so that an optimal level of bioactivity is sustained. Overall biodegradation is faster and more complete.

Sodic Soils and Alkali Seepage

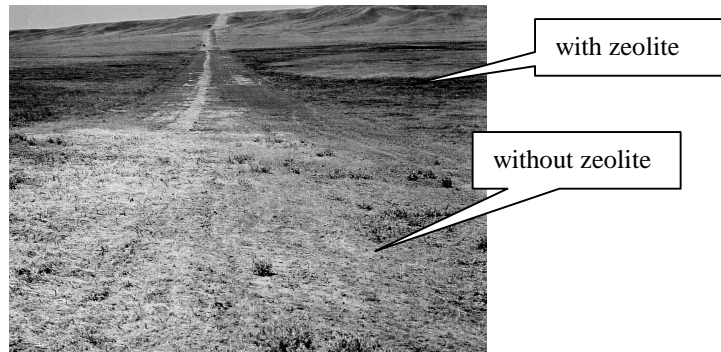
Rotospiking 5 to 10% into sites affected by saline or sodic conditions improves germination and sustained growth of grasses and grains.

SODIC SOIL SITES INCORPORATION BY ROTOSPIKING



Pipelines

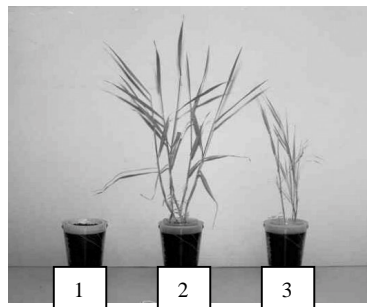
PIPELINE RIGHT-OF-WAY APPLICATION TO DISTURBED SOILS



Soil Sterilants

The persistent toxicity of soil sterilants, many of which are still showing their effectiveness years after application, has resulted in many sites where remediation has been particularly difficult. Often the only solution is to remove contaminated material to landfill and replace it with clean topsoil.

Reclamation of the soil by a 20% incorporation of REMEDIATOR into the top 6 inches of soil has produced some remarkable results. Bench scale demonstration of the germination and growth of barley in such soils indicates the immediate mitigation of the toxic effects of such chemicals.



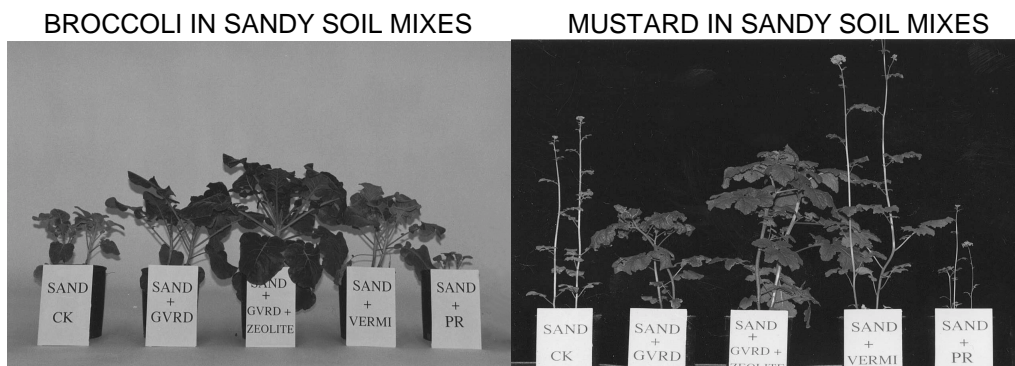
1. The soil sterilized by defoliants. Barley seeds would not even germinate.
2. The same soil with a 20% zeolite incorporation. Healthy germination and growth.
3. Uncontaminated control soil from the same area. Growth is supported, but at a poorer rate than the remediated site.

Reducing Environmental Impact

Increased utilization of manure and biosolids as a rich source of nutrients is gaining popularity. As application rates increase, there is a concern about the additive effects of toxic components. Salt and heavy metals are the main problems, although fugitive losses of ammonia to atmosphere and nitrogen and phosphate loss to ground water are also a concern.

Biosolids Disposal

Municipalities like the idea of turning biosolid waste into a useful commodity. Toxic ingredients however, reduce the allowable rate and frequency of application. Our work with the Pacific Agri-food Research Centre has determined that the inclusion of minor rates of zeolite in the biosolids mitigates the toxic effects.



Manure Management

Intensive farming practices have put additional pressure on manure management. While nitrogen is a valuable nutrient, it is also an environmental hazard. Ammonia losses to atmosphere produce white haze; ammonium and nitrate losses to ground and surface water contaminate aquifers and waterways. Zeolites hold nitrogen in the soil, moderate nitrification of ammonia and make it available to plants as needed.

Conclusion

The cost of production and distribution of zeolites in North America has hindered their acceptance into many attractive situations. C₂C is committed to providing affordable products and technologies to the market for these remarkable minerals. We are experiencing an ever-expanding knowledge base and with it comes an ever increasing list of opportunities. For environmental problems, a host of solutions based on the attributes of these natural materials is now available.

Biography

LuVerne E.W. Hogg is president and CEO of C₂C Zeolite Corporation, a Calgary based industrial minerals company. Mr. Hogg has over 30 years experience in the exploration and development of industrial minerals. In 1997 he founded C₂C for the purpose of developing zeolite deposits in British Columbia and Nova Scotia and for marketing the technologies and products derived from those operations.