Innovative techniques: zeolite, mycorrhiza, metallurgical waste

2.1 Zeolitic rocks

In the context of a development model that is increasingly interested in recovering and recycling waste materials and debris, need to give greater value to raw materials is relevant and increasingly recognised. These include volcanic origin zeolite rocks used in phytodepuration systems with the aim of improving its output.

There are enormous deposits of zeolite rocks in Italy and geo-mineralogy studies on these rocks span over forty years.

Typical properties

Thanks to their structure and chemical crystallography nature then, zeolites have distinctive chemical-physical properties like:

a) reversing dehydration;
b) selective adsorption;
c) acute and selective ability to cationic exchange (always reversing and not influenced by temperature).

Depending on the type of original sediment and degree and diagenesis environment, zeolites produce:

1) lithoid consistency;
2) micro-porosity texture, connected to the lithological (coherent rock) and structural nature (hollow and channels in the zeolites);
3) specific weight, around double pumice and less than half quartz.

d) The (texture and structural) porosity is “real” as pores communicate with each other and therefore beyond the rock. A dried percolated zeolite, then, absorbs flow water until pore saturation (=water retention), it lets the excess pass easily (=permeability) and returns, after desiccation, to its original state without any structural or textural change.

e) As the structural micro-porosity contains water (up to 20% in weight of the zeolite) that is constantly and perfectly balanced with the external tension of vapour, zeolities at higher temperatures or dry environment, give way with the absorption of heat (=endothermic reaction) part of their water that they regain with the transfer of heat (=exothermic reaction) at lower temperatures or damp environments (these dehydration and hydration processes can only take place when seasons change or when day turns to night).

In general zeolites are colourless or whitish, however sometimes, due to the presence of tiny occlusions of iron oxides or organic substances, they can be flesh-coloured or reddish-brown. Their brightness, although not noticeable, can vary from glassy to mother of pearl or fatty, even to silky in fibrous types.

Concentrated hydrochloric acid decomposes zeolites, with silica separation, generally to a gelatinous state.

Zeolite rock in the soil keeps the level of humidity and temperature constant and distributes this balance to the environment around it.

Zeolities transmit their properties to the rock that contains it according to the type of zeolite and its percentage content.

Classification

Zeolities can be divided into three groups (tab. 1): “fibrous zeolites” have a crystalline structure characterised by tetrahedral rings (Si, Al) O_4, joined in chains lengthened side by side to the crystallographic axle c, “tabular zeolites” and zeolites not included in the previous two groups. The differences among the various groups are verifiable in their internal organisation and different structural dispositions of tetrahedrons influence the morphology and mineralogical characteristics.

Tab. 1. Classification of zeolites

Fibrous zeolites	Tabular zeolites	Other zeolites
Natrolite	Heulandite	Phillipsite
Mesofite	Stilbite	Harmotomo
Scolecite	Epistilbite	Chabasite
Thomsonite		Gismondina
Mordent		Offretite
Laumonite		Erionite
Dachiardite		Gmelinite

Gonnardite Edingtonite		Faujasite

Italian zeolitised rocks mainly contain Chabasite, phillipsite and clinoptilolite (variety of rich heulandite in silica and alkali). Chabasite and phillipsite are present in rocks in Lazio and la Campania respectively between 50% and 10%, clinoptilolite is present in Sardinian rocks with a percentage between 40% and 70%.

Use of zeolitic rocks

Zeolites show lithoid consistency and - given their genesis - generally take a surface position, extend considerable distances (tens or hundreds of square kms) and are very thick (50-100 metres), therefore they are quite inexpensive to extract. Zeolites (also known as 'natural zeolites') are very attractive then to sectors that need vast quantities of high quality and constantly pure material and low commercial costs: Zootechnics (animal food additives, silaging cereals, liquid waste and composting), aquaculture (water purification in fish farms), civil, industrial and agricultural wastewater purification. It is also necessary to remember that zeolites can be used to remove lead, chrome and cadmium from watery solutions, as well as disinfecting these materials when affected by concentrated levels of bacterial liquid waste.

Using zeolitic rock in phyto-absorbent channels

The choice of using zeolitic rock as a medium in phyto-absorbent channels is based on a type of zeolite with high Chabasite content, as opposed to the prevalence of phillipsite. This preference is justified by the fact that phillipsite's high selectivity towards NH4+ can make it compete with the hydrophyte plant roots that grow on the bed. Chabasite, on the other hand, is less selective, succeeds in exchanging the ion ammonium of the water and slowly surrenders it to the plant. This mechanism has a double advantage - on one hand, the rock holds back the ammonium of the water flow and makes it available for the plant roots, and on the other, the roots develop a "regenerating" role towards zeolitic grains, exchanging ammonium with the sour humics that they issue.

2.2 Metallurgical wastes

The adsorbent substratum represents the most appropriate solution, in comparison to vegetation, deposits, fauna and micro-organisms, to hold back the phosphorus in the long run.

In agriculture, interaction between phosphorus and the ground have been thoroughly studied and it was noticed that the fixation of nutrient in the ground includes both the adsorption and precipitation phenomena, although the first - in the long run - clearly has more importance compared to the second. This fixation is generally attributed to Fe, Ca and Al oxides.

An Australian study deduced that removing phosphorus from wastewaters can take place in some types of ground, industrial by-products (metallurgical waste) and adsorbent materials, like zeolite, thanks to the concentrated presence of Ca, Al and Fe oxides in the substrata.

In fact, recent studies on metallurgical waste, from Lucchini steelworks in Piombino, show its significant ability to remove phosphorus.

Using these by-products discarded by the iron and steel industries makes a law necessary on reusing non-dangerous refuse. The Ronchi Decree (D.Lgs. 22/97) and following modifications represents a relevant innovation, because it no longer puts refuse disposal at the centre, but, where possible, its recovery and reuse. Among the particularly important decrees, is the DM 5/2/98 (simplified procedures), where a detailed list of materials not considered dangerous is supplied, that can be recovered and then reused (the refuse's origin, characteristics and practicable activities are specified together with, finally, raw material properties and by-products). The same decree also contains the directives (test of disposal) for assessing the conditions of the material's release, which, in order to be reused, must not exceed regulation values. Attention then moves to the potential pollution of ground and subsoil as well as underground and surface waters, due to meteoric waters percolating on the refuse.

With the aim of determining maximum adsorption, the blast furnace waste and chaff were put in contact with solutions containing large quantities of phosphorus. The experiments came up with the following results concerning adsorption: for the blast furnace waste 3659.5 mgs P/kg waste; for the blast furnace chaff 22259.2 mgs P/kg chaff. The greater ability of adsorption towards phosphorus is attributed to the presence of Ca, Al and Fe oxides that tie to it forming salts that fall and remove phosphorus from the water.

A second series of tests verified the adsorption ability of smaller concentrations of phosphorus.

Results emphasised the steelworks waste's greater potential for removing nutrients, due to its speed, compared to chaff.

As the quantity of incoming P increased, a reduction of pH was observed for both materials and in some cases went over the admissible limit[1].

Based on data found during testing, excellent abilities to adsorb high concentrations suggest the use of materials in presence of effluent of limited capacity and containing vast quantities of phosphorus to be purified, rather than using refinement filters where capacities are high and phosphorus concentrations are low. Saturation time calculated for waste is longer compared to chaff, so regeneration of the tubs is less frequent.

Mycorrhiza plants

Terrestrial vegetation has an aerial part or growth, specialised in photosynthetic fixation activities of carbon, gaseous exchanges and evapotranspiration as well as going into the subsoil with the aim of anchoring to the soil, as well as mediating all chemical, physical and biological relationships with the soil's biotic and abiotic components.

The root system

The extension of a root system is the result of two fundamental processes: growth and ramification. They are simultaneous, not independent and influenced by different factors: presence of hormones, concentration of salts, density of soil, presence of micro-organisms (for example mycorrhiza fungus).

The rhizosphere

The area of contact between the ground and the root system is called the "rhizosphere" and is basically divided into three areas:

1) the endorhizosphere that extends from the surface of the roots to the first internal cellular layers;
2) the rhizoplane or external surface of the roots and part of the ground where the absorption of nutrient substances takes place;
3) the ectorhizosphere that is the volume of ground in immediate contact with the roots of varying sizes according to the type of plant and relative interaction with the ground's microbic components.

The rhizosphere model can simply be represented by a "biological family" represented by the following essential elements:

- ✓ plants
- ✓ fungus

[1] In accordance with the Ministerial Decree of 5 February 1998 the admissible limits of concentration for some polluting elements are: Nitrate 50 mg/l NO3; Fluoride 1.5 mg/l F; COD 30 mg; pH 5.5-12.0.

- ✓ bacteria

In this chain, nutrient substances (mineral salts) undergo primary decomposition by bacteria, while fungus transports them to the roots through which the plant absorbs the food.

In this mutual association with the root system, fungus and bacteria achieve a constant flow of carbonaceous substrata from the plant.

2.3 Mycorrhiza

Mycorrhiza can be defined as a classic case of ‘mutual symbiosis’ between some fungus and plant roots - two living beings are complementary in using resources and mutually benefit from exchanging sugars produced by the plant and nutritional elements absorbed by fungus.

Mycorrhization is a technique, aimed at improving or inducing, the ability to assimilate nutrients from plants.

It is the most common type of symbiosis in nature - over 90% of vegetal species in natural conditions is mycorrhized.

Even remains have been found of fossils confirming the existence of endomycorrhiza 450 million years, at the same time as vegetal on emerged land. Even today in anthropised environments (agricultural fields and urban green) mycorrhiza are often completely or nearly completely absent, probably due to chemical pollution of the ground.

Mycorrhiza have a type of covering or mantle, in the shape of a hypha mesh, that includes or covers the tips of its roots.

A third element that takes part in the cycle of assimilating minerals is bacteria that acts on the primary decomposition of nutrient substances in simpler composts (mineral salts).

Bacteria

Ground is represented by sand, slime, clay, decaying organic substance, air, water and an enormous number of living organisms, estimated at around 10 million per gram of uncontaminated ground.

Inside the “mycorrhizosphere” (environment around the mycorrhiza), different micro-organisms interact both directly and indirectly, influenced by the plant and abiotic factors.

The definition ‘Plant Growth Promoting' (PGP) indicates rhizosphere bacteria (Bacillus, Pseudomonas, Phrankia, Streptomices) that can increase plant growth and inhibit development of some Phytopathogenics. These are micro-organisms normally present in agrarian and forest environments that have belonged to plant evolution for around 600 million years.

The enormous genetic variability together with easy adaptability of bacteria and the rhizosphere, allows them to attack and metabolise any substance. Some of these (Mychorrhizal Helper Bacteria) are able to stimulate plant growth by producing phytohormones or other antibiotic composts that limit the growth of antagonist micro-organisms.

There are however also bacteria that inhibit Mycorrhization.

Nitrogen-fixers and phosphate-litic bacteria also interact with Mycorrhization processes and alter nutrient mineral availability in the ground.