Preliminary investigations into the characteristics and potential uses for Ngakuru zeolites

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Abstract

The Ngakuru zeolites are located about 20 km south of Rotorua and comprise a number of deposits dispersed along several fault lines. Relatively recent volcanic activity (250,000 years ago) resulted in ash depositions that vary in depth and mineralogy. Subsequent variable thermal alteration intensities generated predominantly clinoptilolite and mordenite zeolites with a range of physical characteristics.

Typically the zeolites have low density (650 kg/m^3), have high liquid (60% of dry weight) and odour absorption characteristics, and a high affinity for soluble cations (CEC $\geq$ 100 meq/100 g).

Traditional kitty litter and oil absorbency markets are being expanded. New opportunities in waste and potable water treatment, organic and synthetic slow release fertilisers, use as a light weight aggregate for speciality concretes, and pozzalome activity are currently being researched.

Introduction

In 1989 Resource Refineries Ltd was established as a mechanical processor of industrial minerals. Aluminium dross, copper slags, fertilisers and plate glass were crushed and screened whilst various other materials were processed under contract. In 1995 expansion strategies were developed that included processing and marketing zeolite.

Investigations into the size, type and location of New Zealand zeolites revealed that the Ngakuru zeolites, situated about 20 km south of Rotorua, held considerable promise. A permit to extract zeolite was secured in 1998 and soon after an operational quarry and a processing plant at Tokoroa were purchased from the FERNZ group of companies. More recently another quarry has been opened that contains a strongly altered zeolite. All zeolite operations have now been grouped under NZ Natural Zeolite umbrella which is a fully owned subsidiary of Resource Refineries Ltd. One of the company's key objectives is to eliminate processing inefficiencies in order to reduce retail prices but maintain profitably.

The resource

The Ngakuru zeolites are hydrothermally altered tuffaceous lacustrine sediment beds up to 45 m deep and are exposed intermittently along several fault lines. Each deposit is thermally altered to various degrees; deposits are usually small and difficult to commercially quarry. However, when all the resources are combined a commercial industrial mineral processing proposition becomes possible.

Zeolites are a unique 3D lattice work of aluminium and silica that share an oxygen molecule thereby generating a relatively large internal negative charge. In excess of 95% of this charge or cation exchange capacity (CEC) and the surface area originate in the internal lattice work. The predominant zeolites present at Ngakuru are mordenite (40 to 80%) and clinoptilolite (20 to 60%) with some cristobalite (0 to 10%) also present.

When compared with zeolites of continental origin (2,000,000 years old) the Ngakuru zeolites are relatively young (250,000 years old) which gives them unique characteristics. When dried they absorb relatively high volumes of liquid (100g zeolite absorbs 70 g liquid) with odour absorption also very high. CEC and internal surface area range from 40 to 110 meq/100g and 34 to 138m^2/g respectively and seem to depend on the degree of thermal alteration. Deposits that are strongly altered are stable after immersion in liquid and do not collapse into constituent clays whilst those that are less strongly altered are not suitable where mechanical strength is important.

In practical terms the high water absorbency of zeolite influences drying and processing costs. The native water content of zeolites is normally about 50% which has to be reduced to less than 10% for successful crushing and screening. Drying, processing and storage become costly procedures when a 12 month supply of material is required. It is anticipated that in the near future significant cost savings can be made in the pre-processing area.

Occluded salts often block the internal channels of the lattice-work, and removal of this material may enhance the CEC of

the zeolite which would assist where cation adsorption is of importance. A preliminary study identified that pre-treatment of zeolites for 30 minutes in warm 0.5 M alkali, acid or salt solutions improved CEC by up to 70%. Research on intensity, duration and frequency of alternate acid and alkaline washes to enhance CEC is required. A further study determined that after 10 washes with 2 M HCl the physical stability of the zeolite was not detrimentally influenced. Such information paves the way for reuse of zeolite under a range of conditions.

Current and potential markets for Ngakuru zeolites

(a) The less strongly altered zeolites are sold under the Blue Pacific label and are particularly suitable for liquid and odour absorption:

- Kitty litter – the white zeolite chips are well established as a kitty litter of NZ origin. Odour and liquid absorption of the chips are excellent. An excellent clumping litter is also produced
- Oil/Hazchem spill absorbent – the granular absorbent market is increasing in size, probably a result of increased environmental awareness. Recent research determined that zeolite saturated with oil retained more hydrocarbons than many other granular absorbents when subjected to the standard landfill leaching test.
- Odour absorbent – Blue Pacific zeolite when placed in a porous container or left in a bowl will readily absorb room, cooking and smoke odours.
- BBQ absorbent – material sourced from Ngakuru are the most cost effective fat and odour absorbers marketed by the BBQ industry. An important extra is that flammability of fat-saturated zeolite is low
- Ammonia absorption – when combined with nitrogenous composts it will absorb ammonia and odours. Similar effects are recorded when used in animal/bird housing.
- Soil remediation – fine zeolite added to light soils at 12.5 tonne per hectare increased yields of maize silage and maize grain by 10% in a non-replicated trial. Zeolite added to peat, sandy or pumice soils increases potassium, nitrogen (ammonia absorption) and water-holding capacity of the soil.
- Animal feed additions – a cascade of effects could follow when zeolite is added to livestock rations.
  - i Moulds which grow on most stored grains, silages and several grasses produce mycotoxins which can significantly impair animal performance and production. Preliminary research has identified that Ngakuru zeolites absorb mycotoxins
  - ii Zeolite additions to calf rations improve calf health, reduce the incidence of scours and reduce rearing house odour.
  - iii It is possible to load zeolite with specific cations (trace elements) required for animal production and then feed these to livestock

(b) The strongly altered zeolites are sold under the Zeotec label and are particularly suitable where physical stability is of importance:

- Water treatment. A small, portable wastewater treatment plant is available for use by clients who wish to investigate the feasibility of using Zeotec to treat water. Studies using this plant are starting to generate interesting and practical information on the effects of zeolite particle size, water flow and cation load of water on adsorption rates.
- Potable and farm water – replacement of sand with similar sized Zeotec particles in filter systems results in enhanced iron, ammonia and manganese removal. Saturation of exchange sites eventually occurs after which filtration efficiency will be similar to that of a sand filter.
- Wastewater – a number of studies have been completed on several wastewater streams where Zeotec has absorbed almost all soluble cations. Some applications for use maybe in niche situations where increased water treatment capacity is required for limited periods
- Landfill leachate – a recent study where leachate from a closed landfill was treated with Zeotec generated water that easily satisfied compliance requirements.
- Aquaculture – several large aquariums and crayfish exporters use Zeotec in water filtration systems
- Swimming pools – UK research revealed that replacing sand in swimming pool filters with zeolite removed ammonia and as a consequence reduced chlorine use by 50%. Lower operational costs and less allergenic reactions to chlorine were recorded.
- Surfactant modified zeolites – USA research indicates that the anion absorbing and filtration capabilities of Zeotec can be significantly increased by the addition of long-chain ammonium derivatives to zeolite
- Sports Turf – Zeotec added to sand based sports carpets, golf and bowling greens increases both the nutrient and moisture holding capacity of the turf. Additions of 10% eliminate dry patch and reduce fertiliser and irrigation management inputs.
- Lightweight concrete. Replacement of concrete aggregate with Zeotec chips reduces the mass of concrete by as much as 40%. Tests are continuing on concrete strength and performance.
- Fertilisers
  - i Synthetic – the large internal pore spaces of Zeotec allow particles to be imbibed with concentrated potassium or nitrogen salts. Preliminary experiments determined that the entrapped salts later become available for plant growth.

ii Organic fertilisers – Zeotec is Bio-Gro certified and if nutrient or particularly ammonium loaded wastewater streams can be identified Zeotec can be used to treat the water with the nutrient loaded Zeotec subsequently being used as a slow release fertiliser.

Conclusion

The Ngakuru zeolites are unique in an international sense; they have high cation and physical absorptive capacities, a probable result of their comparatively recent genesis. A series of small deposits which are thermally altered to varying degrees are found along several fault lines in the Ngakuru area. The range of zeolite types present provides the basis of a "boutique" industry where a number of minimal environmental impact quarries can be opened to satisfy various end uses.

The potential uses of zeolite have been expounded for about 25 years and despite huge potential, increases in sales in the western world have been minimal. In the past interest, enthusiasm and investment have not been rewarded by increases in sales volumes with many investments not showing appropriate returns. It is now clear that for success the marketing mix must contain specialist technical support (each client's use is usually unique) and realistic product pricing. The latter requires extensive industrial mineral processing experience.

Not-withstanding this, zeolite represents an interesting and challenging business proposition. As environmental concerns increase reducing demand for chemical use and global warming tests current water supply systems the prospects for zeolite look favourable.

Author

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