

Grain size of activated carbon, and untreated and modified granular clinoptilolite under freeze-thaw: applications to permeable reactive barriers

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ABSTRACT. Permeable reactive barriers are used to adsorb contaminants from soil water. Their fillings are granular materials whose stability under freezing conditions has not been demonstrated. In this research, three granular materials (activated carbon, raw clinoptilolite and a nutrient amended clinoptilolite) were subjected to freeze-thaw cycles at different moisture conditions, in order to simulate their use in permeable reactive barriers in areas of freezing ground. The <250 µm fraction, which will potentially accumulate grain fragments, showed no change for the carbon, but an increase from ~1% to ~3% abundance by volume for the clinoptilolite with modes at 100–200 µm. SEM images show cracks in the zeolite grains, forming fragments of the size observed in the particle size data. These findings may have implications for the long-term permeabilities of reactive barriers operated in areas of freezing ground.

Contents

Introduction	121
Materials and methods	122
Results	123
Discussion and conclusions	124
Acknowledgements	126
References	126

Introduction

Remediation of contaminated sites in many areas containing freezing soils imposes special constraints in terms of remoteness, cost, maintenance and the effects of freeze-thaw cycling (Poland and others 2003; Snape and others 2003), and yet there has been a relative lack of investment in remediation technologies (Williams 2003). Permeable reactive barriers (PRBs) are a relatively new technology that allows the remediation of soil and groundwater via the retention of inorganic contaminants such as metals (e.g. Naftz and others 2002), and either retention or treatment via bioremediation in the case of petroleum hydrocarbons (e.g. Snape and others 2001). The advantages of PRBs are that they are relatively easy to install and maintain, have low energy requirements to operate and can be designed to handle variable flow conditions (Snape and others 2001), all of which are particularly important for remote sites where logistic and financial constraints can be substantial. The granular, reactive materials used in PRBs may be customised to retain contaminants of

concern. For example, some materials, such as the zeolite family of minerals (\pm surfactant modifications), work via adsorption and ion exchange (e.g. Bowman 2003), while others, such as zero valent iron, work via *in situ* manipulation of oxidation-reduction potential (e.g. Vermeul and others 2002). In each case, however, the reactive material has to remain more permeable than the surrounding material in order to allow treated water to flow away down gradient.

Freezing and thawing can have profound effects on moist, granular materials. Stresses imposed by the movement of water, in conjunction with the increase in volume resulting from the phase change of water to ice (Walder and Hallet 1985, 1986), can impose strains that cause fragmentation of grains. Rock types that are porous, foliated or have other structures which make water entry easy, split more readily (Mackay 1999). Zeolite minerals, such as those used in PRBs, have a porous, open framework structure (Newsam 1986). This large effective porosity allows the ingress of water within the grains, with potential damage to the grain upon freezing and thawing. Li and others (2001) noted an increase in the fine (<150 µm) fraction of a zeolite:sand mixture following freeze-thaw. If the effects of freeze-thaw are fracturing of grains and shedding of fine particles, then an overall fining of the grain size distribution can be predicted. The creation of additional fine particles and their movement within a PRB can potentially lower permeability in some places while leading to enhanced

Table 1. Volumetric soil moisture contents of the three materials tested, for the conditions air dry, drained and saturated. Data are presented as arithmetic mean \pm 1 standard deviation, for 5 measurements taken with a Meridian Measurement MPM-160 Moisture Probe Meter (ICT International P/L, Armidale, Australia).

Material	Air dry (%)	Drained (%)	Saturated (%)
PicaCarb GAC	6.8 \pm 0.41	22.9 \pm 1.55	33.8 \pm 0.46
AZC clinoptilolite	4.6 \pm 0.57	13.8 \pm 0.54	45.6 \pm 0.51
ZeoPro clinoptilolite	3.1 \pm 0.78	17.1 \pm 1.32	41.1 \pm 0.33

permeability in others. The hydraulic integrity of the barrier, and thus the residence time of the water being treated, depends on the maintenance of the design particle size distribution of the PRB fillings. Freeze-thaw might also remove surfactant coatings used to adsorb organic molecules (see review by Bowman 2003).

While PRBs are now being used in the Arctic (e.g. Poland and others 2001; Lindsay and Coulter 2003) and Antarctic (Snape and others 2001; Woinarski and others 2003), the effects of freeze-thaw on the integrity of the barrier materials has not been considered. The aim of this study is to determine whether or not freeze-thaw cycling has a measureable effect on the grain size of selected granular barrier materials. Here, we emphasise the analysis of the $<250 \mu\text{m}$ fraction, in order to examine closely for the effects described by Li and others (2001).

Materials and methods

The experimental design consisted of a granulated activated carbon, an untreated clinoptilolite from Australia and a nutrient-amended clinoptilolite from the United States, each with three moisture contents, two freezing conditions, and at least five replicates. This design resulted in the analysis of at least 30 samples of each material. Each experimental condition is discussed in detail below.

These three materials were chosen for examination because they were already under consideration by the Australian Antarctic Division for use in PRBs to trap metals and hydrocarbons at Casey Station ($66^{\circ}17'S$, $110^{\circ}31'E$). The first material was the granulated activated carbon (GAC) product PicaCarb, produced from coconut husks and supplied by Pica Activated Carbon P/L. This GAC was supplied screened to $4 \times 1 \text{ mm}$, with a mean grain size of $\sim 750 \mu\text{m}$. The second was an untreated clinoptilolite from Werris Creek, NSW, Australia, supplied by Australian Zeolites P/L. The rock was crushed and screened, resulting in an angular material, here termed AZC, with a grain size of ~ 0.1 – 1.2 mm . X-ray diffraction analysis showed the AZC to contain quartz, clinoptilolite, orthoclase and anorthoclase as major phases. The third material was ZeoPro, which is a nutrient-amended clinoptilolite with a grain size range of ~ 0.1 – 1.0 mm , supplied by ZeoponiX, Inc (Colorado, USA). X-ray diffraction analysis showed the material to be a mixture of quartz, clinoptilolite, orthoclase and anorthoclase and an unidentified material which may have been an ammonium-based salt.

The three moisture contents were (i) air dry, representing the material either in storage or in use near to the barrier surface where sun- and wind-assisted desiccation can lower moisture contents to dryness, (ii) drained, representing material at field capacity in the vadose zone, and (iii) saturated, representing material below the water table (Table 1). The soil water at Casey Station is slightly saline with a typical conductivity of 1 mS/cm , probably as a result of sea spray from Brown Bay which is upwind of the site. In order to emulate field-realistic ionic strengths and ratios, we supplied moisture to the experimental materials as seawater, filtered at $0.45 \mu\text{m}$ (to prevent algae growth) and then diluted with deionised water from 33 mS/cm to 1 mS/cm .

This experiment consisted of either 0 freeze-thaw cycles (i.e. $\sim 20^{\circ}\text{C}$, for control samples) or 60 freeze-thaw cycles. At Casey Station, Antarctica, there are typically 12 freeze-thaw cycles per year at a depth of 30 cm in the soil (Susan Ferguson, AAD, unpublished data). So, for a projected 5 year design life, PRB materials at that depth would have to withstand 60 freeze-thaw cycles. In the field, freezing and thawing is one dimensional, occurring from the top down in response to solar radiation and transfer of sensible heat from air, soil and runoff. In the soil, lateral expansion is confined by surrounding frozen materials. In order to recreate these conditions, samples were placed in 30 mL HDPE containers, surrounded by a snug polycarbonate sleeve which constrained tightly any lateral expansion. In the PRB at Casey, these materials will be used from 0 to 1.5 m below the surface. However, no attempt was made to constrain vertical frost heave or simulate overburden pressures because the intention was to simulate near-surface environments. The containers were then placed into holes drilled into blocks of R4 insulating building foam. An insulating floor was retained below the samples so that only the top was exposed to the air. Each foam block contained 20 samples. Up to four foam blocks were placed at a time into a Sanyo MIR-253 freeze-thaw incubator. The different treatments were randomised throughout the blocks in order to reduce the effects of any systematic differences in temperature within the incubator.

The incubator can be programmed to cycle through different temperature configurations. Several “dummy” samples consisting of drained Australian zeolites clinoptilolite and incubator air temperature were monitored at 15 minute intervals for a number of freeze-thaw cycles. The warmest temperature (9°C) was chosen because it

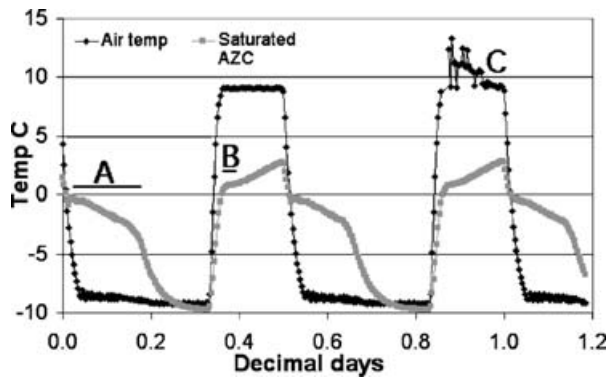


Fig. 1. Freeze-thaw curves for thermistors in the incubator, which was programmed for 60 cycles of 8 hours at -10°C , followed by 4 hours at $+10^{\circ}\text{C}$. Two thermistors were hanging in the incubator airspace, while two were buried in saturated Australian Zeolites Clinoptilolite (AZC) in the insulated blocks. Air temperature ranged from -10 to $+13.5^{\circ}\text{C}$, while sample temperature ranged from -10 to $+3^{\circ}\text{C}$. There is asymmetry in the cooling and heating cycles. The $\sim 3\text{--}4$ hour lag in cooling of the zeolite behind air temperature at position (A) is caused by the slow transmission of sensible heat in the mixed ice/water of the sample pores, plus the absorption of the latent heat of freezing. The shorter (~ 45 minute) lag in the warming of the zeolite at position (B) is caused again by the slow transmission of sensible heat through the sample, but aided by the release of the latent heat of melting. The temperature variations at position (C) were caused by repeated opening of the incubator door.

was realistic of field conditions. The coldest temperature (-9°C to -10°C) was chosen for two reasons. First, Ramos and others (1996) proposed that freezing of soil materials takes place over a range of temperatures, and that as much as half of the water in a clay soil will remain unfrozen at -2°C . The intention was to ensure that most of the sample froze. Secondly, the aim was to attain a temperature within the range -15°C and -4°C , at which freeze-thaw weathering is most effective (Walder and Hallet 1985).

Fig. 1 shows that the change in air temperature and the response of the zeolite samples occurred relatively rapidly, but far slower than the $2^{\circ}\text{C}/\text{minute}$ thermal gradient that Hall and Andre (2001) cite as critical for the onset of grain fragmentation. However, the zeolite temperature response lagged for ~ 4 hours at 0°C to -2°C on the freezing cycle, and at 0 to $+2^{\circ}\text{C}$ on the thawing cycle, due to the latent heat transitions and the time taken for sensible heat to travel through the sample. The exotherm (see Hall 2004) upon phase change from water to ice was not observed, though it may be that the water froze slowly and the evidence of the exotherm effect was subtle. The 8 hour freeze plus 4 hour thaw cycle that was used guaranteed that wet samples were completely frozen and thawed each cycle. Sixty of these 12 hour cycles took 30 days to complete.

At least five (and up to 15) replicates were made of each experimental condition. The particle size distribution of each material was then examined. Grain size analysis

of the GAC using water suspensions (for example laser sizing) or sedimentation techniques (for example x-ray, hydrometer) was problematic because the carbon grains floated in water and alternative liquids were considered. Ultimately, the fines were too difficult to analyse by themselves, but the coarse grains were induced to sink by “waterlogging” in ethanol for 24 hours, then deionised water for 24 hours, prior to analysis in a settling tube. The AZC and ZeoPro clinoptilolite samples were wet sieved at $250\ \mu\text{m}$, and the grain size of the $<250\ \mu\text{m}$ fraction was analysed five times, using a Malvern LaserSizer optical bench with Hydro 2000g accessory. A particle refractive index of 1.475 (clinoptilolite) and water refractive index of 1.333 were used. The change in the amount of the $<250\ \mu\text{m}$ fraction was measured. Selected zeolite samples were also examined using a JEOL JSM-840 scanning electron microscope, to determine whether or not changes to particle surfaces could be discerned. The grain size data for each material were examined using a General Linear Model (GLM; Minitab Release 13.32), with the variables being moisture (dry, drained, saturated) and freezing cycles (0 and 60 cycles).

Results

The Granulated Activated Carbon (GAC) appeared unaffected by freeze-thaw (Fig. 2), with GLM revealing no significant difference in mean grain size ($F_{2,21} = 0.49$, $p = 0.618$) with moisture content or freeze-thaw cycles.

The Australian Zeolites clinoptilolite (AZC) exhibited a significant interaction between moisture and freeze-thaw (GLM; moisture \times freeze-thaw cycle $F_{2,42} = 4.38$, $p = 0.019$), with a coarsening of the mean grain size of the $<250\ \mu\text{m}$ fraction with freeze-thaw in the presence of water. Fig. 2 shows that the significant differences are that “60 f/t drained” and “60 f/t saturated” have mean grain sizes that are coarser than the other treatments (Fig. 2). Examination of the laser sizer data (Fig. 3) shows that the “60 f/t drained” and “60 f/t saturated” samples increased in mean grain size due to the addition of particles with a modal peak around $200\ \mu\text{m}$. The $<250\ \mu\text{m}$ fraction increased from $\sim 0.4\%$ to $\sim 2\%$ by mass as a consequence of freezing and thawing in the presence of moisture.

There was a significant interaction between moisture and freeze-thaw in the ZeoPro clinoptilolite (GLM; moisture \times freeze-thaw cycle $F_{2,24} = 21.40$, $p = 0.000$), with a coarsening of the mean grain size of the $<250\ \mu\text{m}$ fraction in the presence of freeze-thaw with water. Grain size was significantly larger for “60 f/t drained”, and “60 f/t saturated” compared with the dry samples or those with no freeze-thaw (Fig. 2). Examination of the laser sizer data (Fig. 4) shows that samples with an increase in grain size have resulted from the addition of particles with modal peaks in the range $100\text{--}150\ \mu\text{m}$. The $<250\ \mu\text{m}$ fraction increased from $\sim 1\%$ to $\sim 3\%$ by volume as a consequence of freezing and thawing in the presence of moisture.

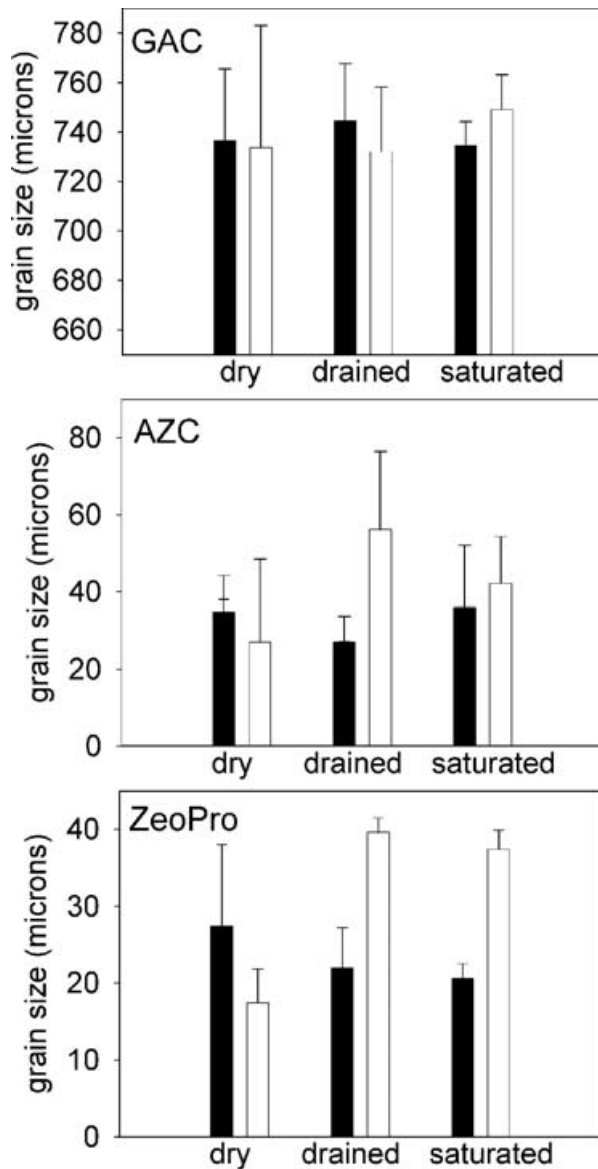


Fig. 2. Box and whisker plots of the mean grain size data for the three materials, for each of the treatments. The bars represent the mean value; the whiskers represent one standard deviation. Black bars represent 0 freeze-thaw cycles; white bars represent 60 freeze-thaw cycles. Note the different scales for each material.

Seventy-one SEM images were made of the AZC and ZeoPro before and after freeze-thaw. There were few discernible changes in the AZC grains following freeze-thaw, although Fig. 5 shows that weaknesses in the particles do exist following freeze-thaw (compare Figs 5 and 6). Similarly, the ZeoPro grains exhibited evidence of micro-cracks propagating through the grain surfaces (compare Figs 7 and 8). In each case, the weaknesses observed and grains produced were in the order of 50–500 μm , consistent with the modal peaks observed in the laser sizer grain size data (Figs 3 and 4).

Discussion and conclusions

There are two main findings from this study. The first is that the grain size of the coconut husk GAC appeared to

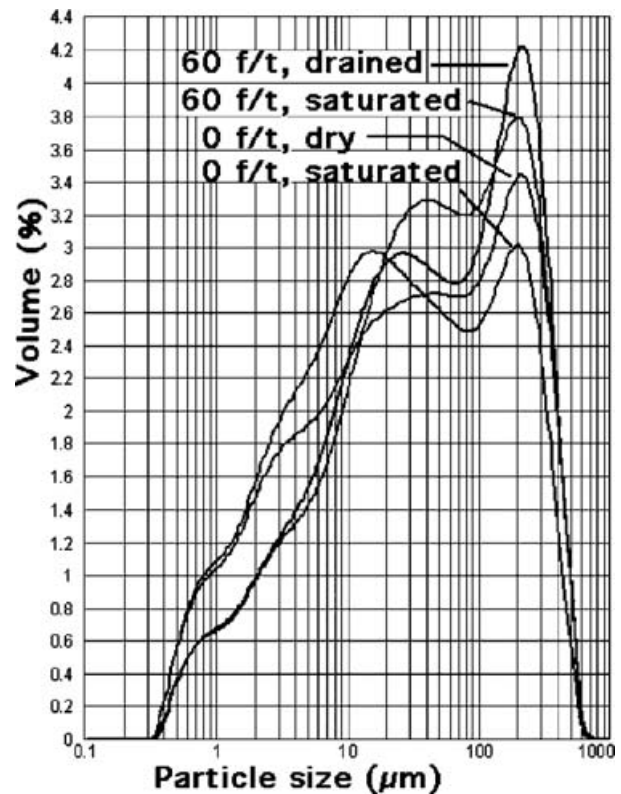


Fig. 3. Grain size of the $<250\ \mu\text{m}$ fraction of four treatments of Australian Zeolites clinoptilolite. Samples that were wet and subjected to freeze-thaw revealed the addition of fragments of $200\ \mu\text{m}$ size, shifting the mean grain size of the $250\ \mu\text{m}$ fraction from $\sim 35\ \mu\text{m}$ to $\sim 50\ \mu\text{m}$. Each curve is an average of 25 measurements made on five samples.

be unchanged with the action of freeze-thaw at a range of moisture contents from 7–34%. However, this finding may not be robust because it was based on measurements of the grain size of the $>250\ \mu\text{m}$ fraction only, which had much scatter about the mean in the measurement data (Fig. 2) and subtle changes to the fine grain fraction may have been subsumed within this variability. However, observations of the material in the sample containers following freeze-thaw revealed no apparent change, consistent with the grain size data reported above.

The second finding is that measurement of the $<250\ \mu\text{m}$ fraction of the two zeolites revealed an addition of material with grain sizes with modes of occurrence around $200\ \mu\text{m}$ (AZC) and $150\ \mu\text{m}$ (ZeoPro), which coarsened the respective mean grain size of the fine grain fraction. The ZeoPro exhibited a slightly stronger change in grain size than the AZC (Figs 2; 4) which is reflected in the larger F statistic for the ZeoPro ($F = 21.40$) versus the AZC ($F = 4.38$). The measured change in the ZeoPro is consistent with the development of cracking observed under SEM (Figs 5–8). The effects were only observed in materials with the combination of moisture and freeze-thaw cycling, consistent with long-held notions that materials must contain water in order to be damaged by freezing (for example Ritchie 1972). Our study confirms that these zeolite materials can be stored

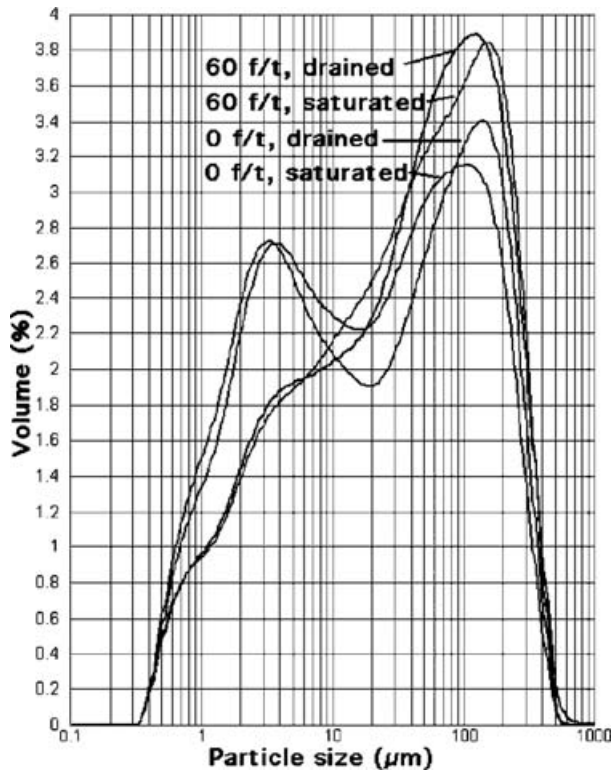


Fig. 4. Grain size of the <math><250\ \mu\text{m}</math> fraction of four treatments of ZeoPro clinoptilolite. Samples that were wet and subjected to freeze-thaw shifted mean grain size from $\sim 15\ \mu\text{m}$ to $\sim 30\ \mu\text{m}$ via the addition of fragments of 100-150 μm size. Each curve is an average of 25 measurements made on five samples.

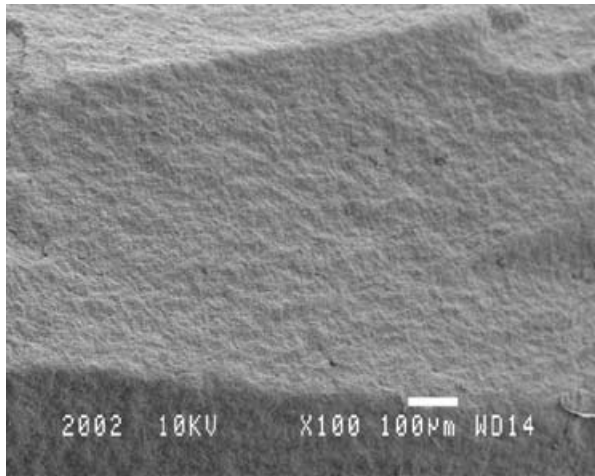


Fig. 5. A selected grain of AZC prior to freeze-thaw, showing a robust mineral surface.

dry at ambient temperatures in freezing environments, without ill-effect to the grains. Interestingly, the effects of freeze-thaw on moist samples were marginally greater for the drained zeolite, than the saturated zeolite. This pattern was observed in the zeolites sourced from both Australia (AZC) and the United States (ZeoPro). Why this was so is not known; temperature dataloggers in dummy samples confirm that both drained and saturated samples

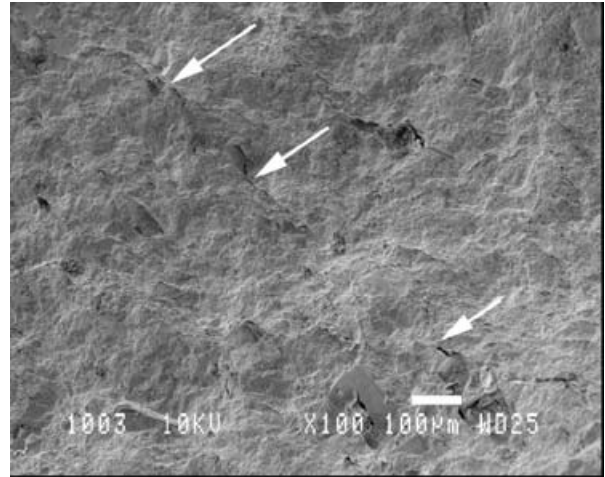


Fig. 6. A selected AZC grain after freeze-thaw, with 400–500 μm -long cracks (arrowed; aligned top left-lower right) visible in the grain surface.

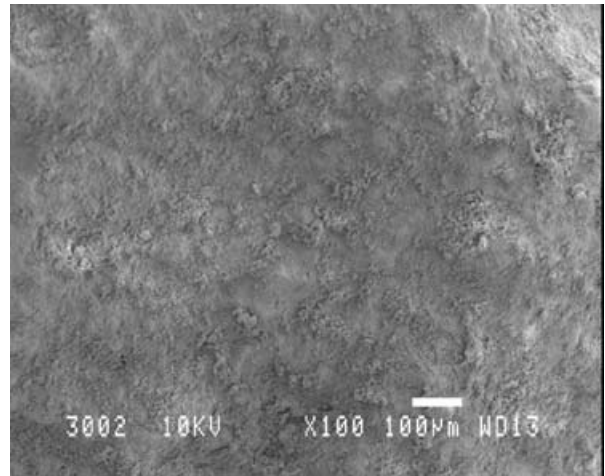


Fig. 7. A selected grain of ZeoPro prior to freeze-thaw, showing an uncracked surface.

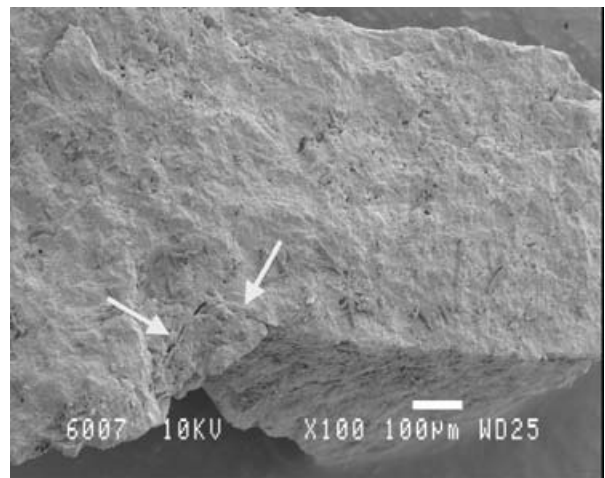


Fig. 8. A selected grain of ZeoPro following freeze-thaw. The arrows show a triangular $230 \times 146\ \mu\text{m}$ wedge of material that has cracked and will spall readily.

underwent similar intensities and durations of freezing and thawing, and all other treatments were similar.

The question remains concerning whether or not these grain size changes are significant for the use of zeolites in PRBs that operate under conditions of freeze-thaw. Since freeze-thaw activity causes the shedding of grains around 100–200 μm size, several consequences may arise for the use of PRBs in areas of freezing ground. During PRB operation, those fine grains may be mobile in the barrier, lodging preferentially in some places and creating zones of reduced permeability. Conversely, zones where fine grains have been washed away will be coarser-grained, enhancing permeability there. In this way, PRBs that were carefully constructed to a design residence time might develop a heterogeneous hydraulic performance, leading to premature contaminant breakthrough and barrier failure. In this experiment, simulating 5 years of PRB operation under Antarctic conditions, the increase in fine grains is minor, with the $<250 \mu\text{m}$ fraction increasing from $\sim 1\%$ to $\sim 3\%$. This increase is consistent with the findings of Li and others (2001, Table 3), who reported that, following 20 freeze-thaw cycles, the $<0.15 \text{ mm}$ fraction of a 85% sand:15% ZeoponiX clinoptilolite amendment mixture increased 1.3% (Li and others 2001) to 1.5% (Li and others 2002) by mass, mainly at the expense of the 250 μm fraction. However in order to determine the significance of this increase in fines for barrier operation and integrity, hydraulics experiments will need to be carried out to examine specifically these potential changes in permeability.

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