Particle Sorting by Repeated Freezing and Thawing

Abstract. *If a heterogeneous mixture of particles of various sizes is frozen and thawed repeatedly, the particles are sorted into relatively uniform groups by size. The movement of particles depends on the amount of water between the ice-water interface and the particle, the rate of freezing, the distribution of the particles by size, and the orientation of the freeze-thaw plane.*

In regions of cold winters, stones often rise to the surface of the ground, fence posts move upwards in their holes, plants are often uprooted, and soil particles are sorted into pockets or layers of relatively uniform size by the action of frost. The upward movement of stones is well-documented, but there is no agreement on the causes of the movement (*1, 2*). This report describes laboratory experiments which demonstrate the effects of direction of freezing, rate of freezing, and shape and size of particles on their movement during repeated freezing and thawing, and the effect of a moving plane of freezing upon the migration of individual particles.

The basic test material was a noncohesive mixture of rounded sand grains and gravel, ranging in size from 0.074 to 7.0 mm in diameter, and a fine fraction (<0.074 mm) composed of crushed quartz. Freezing cabinets were placed in cold rooms maintained at −5°, −10°, and −20°C. The rate of freezing or thawing was regulated with a heating tape situated opposite the freezing front. Freezing rates were determined by thermocouple measurements at the contact between the sample and the cabinet wall. After the sample had been subjected to the required number of freeze-thaw cycles, horizontal layers 15 mm thick were examined, and the number of particles finer than 0.074 mm in each layer was determined by sieve analysis. The difference in concentration, by weight, of these particles in successive layers indicated the amount of particle migration produced.

One set of experiments was designed to simulate conditions in regions of the earth where the soil both freezes and thaws from the surface. The thermally controlled cabinet of Schmertmann (*3*), provided these conditions. Freezing rates ranged between 0.6 and 1.4 mm per hour; the thawing rate was 6.0 mm per hour. Preliminary experiments with tetrahedrons, 2.5 cm in height, and glass marbles, 2.5 cm in diameter, showed that coarse particles moved upward, whether they were buried just beneath the sand surface or 12 cm below. The tetrahedrons moved upward faster than the marbles. Analysis of the grain size of the sand showed that 20 freeze-thaw cycles increased both the number of fine particles in the lower part of the sample and the number of coarse particles near the surface. The term "vertical sorting" is proposed for this type of movement in the freeze-thaw layer (*4*). The rate of downward movement of sand particles finer than 0.074 mm was 0.2 to 0.3 percent (by weight) per cycle.

Samples which exhibited vertical sorting also showed changes in volume which were related to the percentage by weight of the different grain sizes, and were inversely proportional to the rate of freezing. The more unsorted the mixture, the larger the volume change due to freezing and thawing.

In extremely cold regions, the layer above the perennially frozen ground freezes from the bottom as well as from the top, and thaws exclusively from the surface. The cabinet designed to study this type of freezing was composed of two Lucite cylinders of equal height (15 cm) and 12.5 and 15.0 cm in diameter, respectively, placed one inside the other, and attached at the bottom to an aluminum plate 2.5 cm thick. The air space between the cylinders insulated the sample, and the cylinders were covered with a wooden box containing a heating tape. A sample of sand, 7 cm high, was placed in the inner cylinder, which was then filled with water to a depth of 5 cm above the surface of the sample.

When the freezing line advanced upward from the bottom, the differential movement of particles created by ice growth at the ice-water interface affected the soil particles below the freeze-thaw plane as well as above it (Fig. 1). This mechanical "shaking" seemed to be responsible for the upward migration of coarse particles and the downward migration of the finer particles in the unfrozen layer, for which the term "mechanical sorting" is proposed. Sieve analysis showed that particles finer than 0.014 mm moved downward 0.1 percent (by weight) per cycle. Under the same conditions, glass beads showed a downward migration of 1.0 percent per cycle, suggesting that an important factor in this type of sorting is the shape of the particles. It is also possible that this phenomenon is related to the thickness of the sample used.

The downward migration of fine particles (<0.074 mm) produced a layer 5 mm thick when the freezing plane moved at a rate of 0.1 mm per hour for 1 week (Fig. 1). Hence, layers can be produced in the ground by freeze-thaw action as well as by irregularities of the original deposition. The same type of vertical sorting can be observed in the freeze-thaw layer above perennially frozen ground, as shown in Fig. 2. Gravels deposited by man in Alaska show sorting after 15 to 20 cycles of annual freezing and thawing. Vertical sorting is not necessarily uniform throughout the layer; because particles migrate at different rates, areas of both fine and coarse particles may appear at the surface.

In regions of intensive seasonal frost or perennially frozen ground, the soil freezes and thaws laterally in places such as riverbanks, retaining walls, culverts, ditches, and terraces. The cabinet designed to simulate these conditions consisted of a rectangular plywood box waterproofed with shellac, measuring 15.0 by 12.5 cm, and 12.5 cm in height, with one side replaced by an aluminum plate which acted as a cooling front. Heating tapes in the opposite side and in the cover were used to regulate the rate of movement of the freeze-thaw plane between 30 and 42 mm per hour. Thermocouple readings in the soil indicated that a vertical freeze-thaw plane was produced. The sample was the same as used in

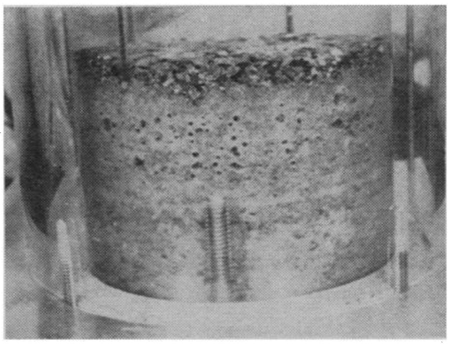

Fig. 1. Side view of cabinet, after seven freeze-thaw cycles, in which freezing was effected from the bottom upward. The sample was frozen at a rate of 0.6 mm per hour, and thawed at approximately 6.0 mm per hour.

the previous experiments, containing 14 percent by weight of fine particles (<0.074 mm). Water was added to saturate the sample.

After 22 cycles of freezing and thawing, the sample was divided into 9 horizontal sections. Sieve analysis showed that particles migrated in front of the freezing plane and that the percentage of finer particles, by weight, increased from the top downward as well as away from the freezing plane. The term "horizontal-vertical sorting" is proposed for this; it occurs in naturally deposited materials in the freeze-thaw layer (*4*) and should also be found in seasonally frozen soils. The shape of the path followed by the particles seemed to be determined by the rate of freezing and by the gravitational force acting on the particles; but this point requires further experimental verification. As in the previous experiments, the volume change was inversely proportional to the rate of freezing.

The actual migration of particles in front of a moving freezing plane was experimentally demonstrated in the cabinet designed for studying freezing from the bottom. Freezing was effected at the contact between the inner cylinder, in which distilled water had been placed, and the aluminum base plate. As the horizontal freezing plane was raised (between 0.2 and 7.0 mm/hr), 20 grams of particles of different sizes were placed on the interface. After freezing the mixture upward 1 cm, those particles that had not been engulfed by the ice were removed by siphoning; the percentage of particles carried was expressed on the basis of weight. The fine particles were carried to the top leaving streams of bubbles trapped in the ice beneath them, while the coarser particles were engulfed by the ice close to the seeding position. Evidently, a moving interface of ice and water can exclude particles located in its path. Various materials were tested, including particles of SiO_2, of the same size but different shapes (glass beads, broken glass, and quartz), and particles of different materials (calcite, rutile, quartz, shale, and mica) which also differed in shape. Some of the results are shown in Fig. 3.

Side freezing is produced in nature around large particles or concentrations of particles which migrate upward and become slightly exposed at the surface. Such particles are better heat conductors than the surrounding finer materials, and initiate freezing from the sides (*2*, *6*). The effect of repeated side freezing and thawing was demonstrated by placing sorted layers of particles in aluminum pans and alternately placing them in cold (−20°C) and warm (+20°C) rooms so that the soil froze mainly from the sides. Vertical sorting was changed into horizontal-vertical sorting regardless of whether the layers were dome-shaped or flat. This can be explained by the fact that the freezing front pushes the soil particles toward the center of the pan, forming a mound. Coarse particles in the upper layers roll from the top of the mound toward the edge of the pan, thus creating sorting.

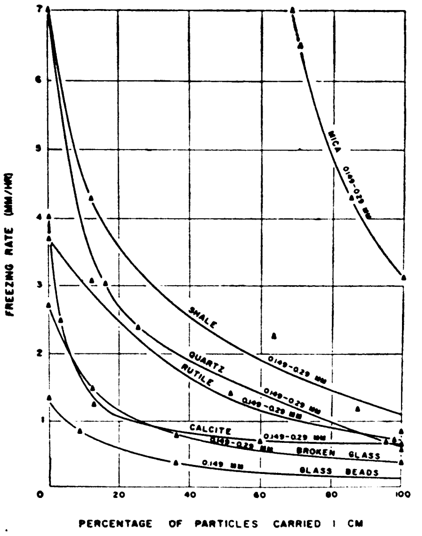

Fig. 3. Percentage, by weight, of glass beads (0.14 mm in diameter), calcite, broken glass, rutile, quartz, shale, and mica particles (0.14 to 0.29 mm) carried 1 cm at different rates of freezing.

Fig. 2. Profile of vertical sorting in flat terrain in which a "boulder field" is forming (Thule area). The scale rests at 25 cm below the level of perennially frozen ground.

The results of these experiments indicate that particle migration in nature is dependent on certain conditions.

1) The rate of freezing. Horizontal-vertical sorting is produced experimentally with freezing rates of 30 to 42 mm/hr. Natural freezing rates range up to 40 mm/hr. Vertical sorting has been produced with freezing rates of 0.6 and 1.4 mm/hr and a thawing rate of 6.0 mm/hr.

2) The size, shape, and distribution of particles. Fine particles (<0.1 to 0.5 mm in diameter) migrate when the freezing rate is either high or low; coarse particles (>1.0 mm) migrate only if the freezing rate is low. An important factor may be the area of contact or the pressure of the particle on the interface.

3) The direction of freezing. It is evident that particles become sorted by the cyclic effect of a freeze-thaw plane; the particles move away from the freezing point. For vertical sorting to be changed to horizontal-vertical sorting, either large particles must be present and partially exposed at the

surface, so that the adjacent soil will freeze and thaw in a non-horizontal plane, or non-uniform vertical sorting must exist.

4) The amount of moisture at the freezing plane. In materials deposited by man, the amount of sorting is directly proportional to the moisture content of the soil (*7*). The actual presence of a layer of water between the ice front and the particle was proposed by Taber (*8*) but still remains to be demonstrated. This water would have to be continuously replenished as the ice advanced, moving the particle in front of it. If the water layer froze faster than it was replenished, the particles would be trapped by the ice. It is reasonable to assume that the layer of water would be more easily and rapidly replenished in the presence of small, rather than large, particles. This would account for the fact that coarse particles move only when the rate of freezing is low.

The results of these experiments may be important in determining the susceptibility of materials to frost over long periods of time. Evidently, the chances of frost-heaving or formation of ice lenses will increase in proportion to the concentration of fine particles. On the other hand, it may be predicted that the soil adjacent to a retaining wall will have a tendency to become less susceptible to the formation of ice lenses as fine particles move away from it.

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References and Notes

1. C. Troll, *Geol. Rundschau* **34**, 545 (1944); L. Washbur, *Geol. Soc. Am. Bull.* **67**, 823 (1956); A. Hamberg. *Geol. Foren. Stockholm Forh.* **37**, 583 (191 → G. Lundqvist, *Geogr. Ann. Stockholm* **31**, 335 (1949); ———, *Geol. Foren. Stockholm Forh.* **73**, 505 (1951).
2. A. Cailleux and G. Taylor, *Cryopédologie Etude des Sols Gelés* (Herman, Paris, 1954), p. 58.
3. J. H. Schmertmann, U.S. Army Snow, Ice and Permafrost Establishment, Corps of Engineers, *Tech. Rept. 50* (1958).
4. A. E. Corte, U.S. Army Cold Regions Research and Engineering Laboratory, Corps of Engineers, *Research Rept. 85*, part I (1961), part II (1962); also *Highway Res. Board. Bull. No. 317* (1962), pp. 9–34; *No. 331* (1962), pp. 46–66.
5. ———, *J. Geophys. Res.* **67**, 1085 (1962).
6. S. Taylor, thesis, Univ. of Minnesota (1956), p. 189.
7. A. E. Corte, unpublished data.
8. S. Taber, *J. Geol.* **38**, 303 (1930).
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Sodium Perxenate Hexahydrate

Abstract. *Sodium perxenate hexahydrate ($Na_4XeO_6 \cdot 6H_2O$) has been identified from study of its crystal structure by x-ray diffraction. The perxenate ion (XeO_6^{-4}) has the shape of a regular octahedron with the Xe–O bond distance 1.84 Å.*

Some hydrated sodium salts of xenon in the +8 oxidation state were produced by Malm, Holt, and Bane (*1*) by hydrolysis of XeF_6 in the presence of sodium hydroxide. Crystal data were reported (*2*) for three phases produced in this way. By determination of the crystal structure one of these phases is $Na_4XeO_6 \cdot 8H_2O$, containing perxenate ion (XeO_6^{-4}) in the shape of a regular octahedron (*3*).

We have produced another salt; this is characterized as $Na_4XeO_6 \cdot 6H_2O$ by determination of the crystal structure. We find the same shape for the perxenate ion with dimensions close to those reported in the work on the octahydrate (*3*). This hexahydrate is not one of the phases reported by Siegel and Gebert (*2*).

The crystals of $Na_4XeO_6 \cdot 6H_2O$ were obtained from the reaction of pure xenic acid (aqueous XeO_3) (*4*) and sodium hydroxide. When 0.100 ml of 0.208*M* XeO_3 (aq) and 0.060 ml of 6*M* NaOH were mixed the resulting solution was pale yellow. After one day in a refrigerator at 5°C, crystals grew as very thin fragile sheets. The production of crystals from the reaction is much more rapid at elevated temperatures, about 60°C, but at this higher temperature the product is the octahydrate. It was identified by its cell dimensions which we measured as a = 11.864, b = 10.426, and c = 10.358 Å (each ± 0.005 Å), in agreement with the previous work (*2, 3*).

The hexahydrate is much less stable than the octahydrate. The x-ray study was made of crystals sealed in thin-walled glass capillaries containing some of the mother liquor. Most crystals survived only a few hours in the capillaries, and several preparations were necessary before adequate data were obtained. Photography of one crystal by the Weissenberg technique gave some preliminary information. Intensity data with MoKα radiation were gathered by direct counting with a scintillation counter for about 1250 reflections (including about 250 absent because of the space group) on one or more of 10 different crystals. At higher angles many of the reflections with mixed (even and odd) indices were too weak to be observed reliably. The determination of the structure was based on 491 reflections from one or another of 5 different crystals, including 14 reflections which were assigned zero intensity. These crystals were 0.3 mm or less in the largest dimension, with thicknesses too thin to be measured with our microscope. Experiments by a technique described elsewhere (*5*) showed that absorption reduced some intensities about 20 percent, but was negligible for most of the data.

The crystals are orthorhombic, space group *Pbca*, with $a = 18.44 \pm 0.01$, $b = 10.103 \pm 0.007$, and $c = 5.873 \pm 0.005$ Å. The density is calculated as 2.59 g/ml with four molecules per unit cell. The crystals were observed to sink in ethylene bromide (density 2.17 g/ml). Xenon atoms are on centers of inversion at the origin and face centers. All other atoms are in general eight-fold sets of positions.

All atoms (except hydrogen, which is not detected with these data) were recognized in the Patterson function. The main features of the structure never changed during the refinement process which was circuitous because change of sign of several of the coordinates has little effect on most of the intensities and because strong correlation among some of the parameters results from pseudosymmetry of the structure. Refinement by least squares eventually reduced

$$R = \Sigma || F_{obs} | - | F_{calc} || / \Sigma | F_{obs} |$$

to 0.072 with the atomic parameters listed in Table 1. Standard deviations of coordinates correspond to 0.01 Å for sodium and 0.02 Å for oxygen. A three-

Table 1. Atomic coordinates and thermal parameters in $Na_4XeO_6 \cdot 6H_2O$.

Atom	x	y	z	B, Å²
Xe	0	0	0	(0.85±0.04)*
Na(1)	0.009	0.164	0.492	1.4±0.2
Na(2)	.252	.155	.539	1.7±0.2
O(1)	.060	.005	.252	1.2±0.2
O(2)	.064	.115	.854	1.8±0.4
O(3)	.951	.136	.127	1.0±0.4
O(W1)	.169	.200	.242	1.6±0.3
O(W2)	.339	.183	.836	1.5±0.3
O(W3)	.192	.518	.242	2.2±0.4

*Isotropic B equivalent to average of anisotropic temperature factor.