Reports

Sodium Chloride: Modification of Crystal Habit by Chemical Agents

Abstract. *Microscopic investigation of drops of brine evaporating in air revealed crystal forms of sodium chloride other than the cube, when cysteine, creatinine, papain, monosodium glutamate, sodium hexametaphosphate, a combination of sodium hexametaphosphate and aluminum salt, or aluminon were added to the brine in small amounts. Some of these have a definite effect in parts per million concentration.*

The many investigations of materials effecting a change in the crystal habit of sodium chloride as it crystallizes from water solution have yielded surprisingly few results. I have tested (*1*) many compounds for their habit-modifying effect on crystallizing sodium chloride and have found seven agents which appear not to have been reported. An empirical approach was used since no way could be found to correlate reported crystallographic data on compounds known to modify the habit of sodium chloride with those of other compounds.

Almost 500 different organic and inorganic compounds were collected for testing (*2*). In order to screen these materials with sufficient speed and sensitivity the experiments were performed on a micro-scale. Lehmann reported doing this in 1888 (*3*) and Frondel (*4*) also used this procedure in 1940.

The formation of crystals in a drop of evaporating sodium chloride solution may be observed through a microscope and anomalous growth can be detected as it occurs. When the anomaly appeared to be due to the presence of an added impurity, an appropriate batch volume of brine was evaporated in a vacuum to determine whether the effect was consistent and reproducible on a practical scale. The test solution consisted of cold distilled water and an excess of evaporated granulated NaCl of purity better than 99.99 percent. A drop of the clear supernatant solution about 5 mm in diameter was placed on a clean microscope slide held in a mechanical stage on a microscope and observed at low magnification, ×60. The entire drop area was scanned during the course of crystallization, which invariably began in the shallow edges in about 1 minute and was completed in 15 minutes, depending on the relative humidity.

When a familiarity with the normally occurring distortions in the drop of pure brine had been gained, it was possible then to differentiate these from changes due to an added impurity. The following procedure could then be carried out. A particle of solid material (such as cysteine) about 0.1 to 0.2 mm in diameter was added to the edge of the drop, thereby establishing a concentration gradient as solution occurs and the solute diffuses into the drop. Thus a qualitative determination of the effect of different concentrations can be observed. Liquid agents can be added by placing a droplet, with a diameter equivalent to that of the solid additive, adjacent to the brine drop and uniting them with a clean needle.

When a material is found which has an effect on the crystal habit, it is tested further in a 2-liter vacuum distillation apparatus fitted with a stirrer and heated with a mantle. Pressure is reduced to maintain a boiling point around 90°C. One liter of pure brine and 0.01 percent by weight of the test material are placed in the flask and the distillation rate is adjusted to remove 400 ml of distillate in 30 to 45 minutes after the first drop of distillate appears. If a change in habit is observed in the dried crystals removed after the distillation, further distillations, with reduced concentrations of modifier, are made to establish a minimum concentration.

An extensive search of the literature revealed only 12 known agents that modify the crystal habit of sodium chloride. Buckley (*5*) mentions urea, cadmium salts, and the chlorides of zinc and manganese as causing the formation of octahedra. Ferrocyanides have been used as anti-caking and habit-modifying agents (*6*). Kaufmann (*7*) has observed a formation of combinations of cube (100) and octahedron (111) resulting from the action of caustic soda, soda, boric, phosphoric, and hydrochloric acids. Furthermore, the addition of mercuric chloride causes combinations of the cube (100) and dodecahedron (110), and antimony chloride causes a combination of cube, octahedron, and dodecahedron.

The greatest effect of the known agents modifying the crystal habit of

Fig. 1. Dendritic growth of NaCl crystals.

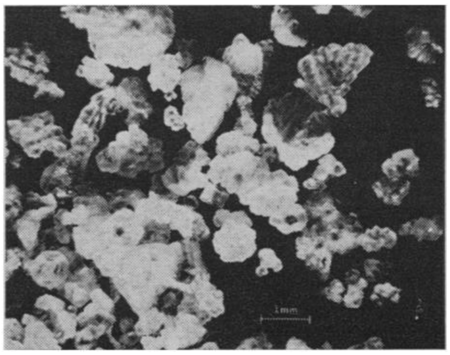

Fig. 2. Basket-shaped crystals of NaCl.

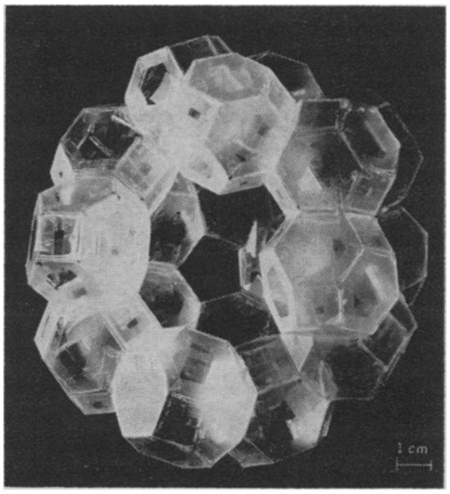

Fig. 3. Model of basket-shaped crystals.

sodium chloride is that of ferrocyanide salts. Concentrations as low as 10 parts per million cause the formation of vicinal (110) faces on (100) planes, thus preventing strongly bonding salt bridges from forming between contiguous crystals. (This is the basis for the anti-caking patents.) At higher concentrations growth layers on (100) are suppressed, and the 12 edges extend themselves around concave cube faces to form skeletal cubes. At still higher concentrations edge growth, as well, is suppressed and the eight corners extend, forming spiky star-like crystals. This last effect forms the basis of the patents on sodium chloride of low-bulk density.

On moist salt crystals drying in air, ferrocyanide salts at very high concentrations cause dendritic growth (Fig. 1). These dendrites are cryptocrystalline extensions of cube corners and grow to lengths of 2.5 cm or more.

Seven effective habit-modifying agents reported here are cysteine, creatinine, papain, monosodium glutamate, sodium hexametaphosphate, a combination of sodium hexametaphosphate and an aluminum salt, and aluminon. The first five agents cause the formation of octahedra. Aluminon causes the formation of very finely divided octahedra, and if there is contamination by an aluminum salt the crystals are colored pink.

The most interesting modifier of crystal habit was the combination of sodium hexametaphosphate with a soluble aluminum salt. When a soluble aluminum salt was present in the system the formation of octahedra resulting from the action of sodium hexametaphosphate was suppressed and cubic crystals formed. However, the two agents in proper ratio in the vacuum evaporator yield in quantity coarse crystal aggregates of sodium chloride shaped like baskets (Fig. 2).

These bulky basket-shaped crystals are aggregates of a geometric solid described by Kelvin (*8*) as regular tetrakaidecahedra. This 14-faced combination is a cubo-octahedron with eight hexagonal (111) faces and six square (100) faces. All edges are equal in length. The aggregate structure is probably derived by accretions of tetrakaidecahedra as in twin position. When in this position the joined (111) faces have a common edge (110) and the adjacent (100) faces have a common edge (001). A model was made with this orientation of the units and a striking similarity to the actual crystal aggregate was found (Fig. 3).

The possibility exists that since (111) faces consist of lattice planes containing, at any given instant, all sodium or all chlorine atoms and other lattice planes alternate sodium-chlorine-sodium, the attractive forces between (111) faces are greater than those between (100) faces. That crystal growth by accretion on similar parallel planes is probable was shown by Schubnikov (*5*, p. 247).

The combination of microscope screening and vacuum evaporation has been found to be a useful technique in this specific application. It would seem to be useful in other crystal-growing processes either to select agents for use in growing better crystals or even to determine contaminants causing poor crystallization.

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References and Notes

1. I thank International Salt Company, Clarks Summit, Pa. for supporting this research and for permission to publish.
2. I thank Professor P. Kerr of Columbia University and Professor E. Sargent of Long Island University for opening their reagent shelves to me.
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4. C. Frondel, *Am. Mineralogist* **25**, 103 (1940).
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8. W. Thompson (Lord Kelvin), *Phil. Mag.* **24**, 503 (1887).

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Origin of Oceanic Manganese Minerals

Abstract. *A criterion is suggested for discrimination between ferromanganese oxide minerals, deposited after the introduction of manganese and associated elements in sea water solution at submarine vulcanism, and minerals which are slowly formed from dilute solution, largely of continental origin. The simultaneous injection of thorium into the ocean by submarine vulcanism is indicated, and its differentiation from continental thorium introduced into the ocean by runoff is discussed.*

Since the discovery of the widespread occurrence of manganese oxide nodules on the ocean floor by Murray and his collaborators (*1*) the origin of these aggregates has been extensively debated. Some authors have assumed submarine vulcanism as the main source of the manganese; others have pointed at the depletion of manganese in continental and epicontinental sediments, leading to a net transport of manganese to the ocean floor. This discussion has recently been summarized and implemented by Bonatti and Nayudu (*2*). A review of the present knowledge of the structure and composition of the aggregates has been given by Arrhenius (*3*).

Bonatti and Nayudu (*2*) have stressed the extensive direct and circumstantial evidence for volcanic origin of the main constituents. However, it also appears beyond doubt that a net transport of manganese takes place from the continental shelves into the deep ocean (*4*). Consequently one is led to assume that both of these processes contribute to the accretion of manganese oxide minerals on the ocean floor (*5*). It is interesting under these circumstances to attempt a discrimination between manganese oxides derived from submarine eruptives, on one hand, and oxide minerals composed essentially of manganese derived from weathering on the continents, on the other. Numerous chemical analyses carried out on manganese nodules, primarily from the Pacific Ocean (*5*, *6*) are available as a basis for such an attempt.

It appears evident from observation of glass specimens, which have reacted with sea water, that considerable amounts of ions of the transition elements in their lower oxidation states may be released into solution in sea