Road Salt and My Car Part 1 & 2

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Anyone living in the northern United States should be familiar with the practice of salting the roads this time of year. Big trucks rumble down the road spreading salt on cars, pedestrians, and anything near the road. At particularly heavy salting times, cars become encrusted in salt, and drivers desperately peer out from streaked windshields, hoping that their windshield wiper fluid will hold out, because if it doesn't, a drying windshield can quickly become obstructed with salty road splatter.

So why do we salt the roads?

We salt the roads to prevent ice and snow from sticking to road surface. That is why ideally salt trucks go out at the beginning of a storm. They are trying to set up a slushy, soft barrier between the road and the snowfall. Then the plows complete the real snow removal. If the roads aren't salted ahead of the storm, several inches of packed snow can quickly become icy and difficult to plow.

Why salt?

Sodium chloride (NaCl), or salt, is cheap, readily available, nontoxic, and very soluble in water. When salt is dissolved in pure water, it alters the properties of the water. You might say "of course it does,...the water tastes salty now," but other properties such as vapor pressure, osmotic pressure, and boiling and freezing points change when any solute (salt) is dissolved in a solvent (water).

These are the colligative properties of a solution, and the property that road salt crews exploit is freezing-point depression. The amount of freezing-point depression is directly proportional to the number of dissolved ions in a solution. The simple equation chemists use is

Freezing-point depression = $K_{fp} \times m_{solute}$

Where K_{fp} is the freezing-point depression constant associated with a solvent (for water, it is -1.86 °C/molal), and msolute is the moles of solute per kilogram of solution (molality). You also need to remember that every ion counts toward the freezing-point depression, so a salt like NaCl really provides two ions, Na+ and Cl-.

Take a look at an example. A 0.5 molal solution of NaCl is 1.0 molal in ions. The freezing point of water/salt solution at this concentration is then depressed by -1.86 $^{\circ}$ C (-1.86 $^{\circ}$ C/molal times 1.0). Since the freezing point of pure water is 0.0 $^{\circ}$ C, the new freezing point of our saltwater is -1.86 $^{\circ}$ C. If we double or triple the concentration of NaCl, the freezing point becomes -3.72 $^{\circ}$ C and -5.58 $^{\circ}$ C, respectively.

This explains why a road surface or bridge can remain slushy or unfrozen at freezing air temperatures (assuming the road surface is not warmer that the air).

But can we keep adding salt to water until the freezing point is -50 °C? No. The solubility of salt in water decreases with decreasing temperature. We eventually reach what is called the eutectic point. This is the point at which a solution achieves a maximum salt concentration. Any colder and salt will begin to leave the solution and raise the freezing point. At the eutectic temperature, ice, saltwater, and solid salt exist in equilibrium. For water, the eutectic temperature is -21.1 °C. Therefore salting roads at temperatures below -21 °C is pointless. In reality, -10 °C is the cutoff for road salting for most practical applications.

Until now we've only discussed NaCl, but calcium chloride (CaCl₂) is also used to salt roads. It has a lower eutectic point than NaCl and can work at lower temperatures. Both salts have their advantages, and some ice-melting formulations use a combination of both.

Part 2 -- Road Salt Ate My Car!

Well, all that salt on winter roads has a side effect--rust!

There is a noticeable difference in the amount of rust found on cars in the North (high salt) and cars in the South. After I moved from western New York to Virginia, I took my 1995 Nissan Sentra to get it inspected by a local mechanic. The fierce winters and high levels of salt had taken their toll, and my new mechanic was flabbergasted. He could not believe the amount of rust on the underside of my car.

This is the same car that--after two and half years--had the muffler and heat shield rust completely off the car in separate incidents. The car underwent quite a torture test. It was never in a garage and rarely washed. It was exposed to wet, salty conditions, followed by warm driving conditions, followed again by a splashing of salty water as a I drove through slush puddles. At night, during the winter, the warm, moist car frequently sat in snow that was high enough to touch the bottom of the car.

What was it about these conditions that caused my car to rust so dramatically? What role did salt play, and what is the chemistry behind it all?

Rust Background

Rust is iron(III) oxide (Fe_2O_3); the oxidized form of iron (Fe). It is reddish-brown, brittle, and powdery and does not adhere well to "un-oxidized" iron. The steel in a car is mostly iron.

Iron Oxidation

If oxygen and water can gain access to an iron surface, oxidation (loss of electrons) can take place by the following reactions.

s = solid Fliquid g=gas aq=aqueous or "in water" Anode: 2 Fe(s) \longrightarrow 2 Fe^{2*} (aq) + 4 e² Cathode: O₂(g) + 2 H₂O () + 4 e² \longrightarrow 4 OH- (aq) N et: 2 Fe(s) + O₂(g) + 2 H₂O () \longrightarrow 2 Fe(OH)₂(s)

At what we call the "anode", each iron atom loses two electrons (for 2 Fe, 4 e-), and becomes the Fe^{2+} ion in solution. For this to occur, there has to be a least some water present. The electrons released by iron then travel to the "cathode", where they are grabbed by oxygen (O₂). By gaining an electron, the O₂ is reduced to hydroxide (OH-). The OH- and Fe²⁺ combine in solution and precipitate out as solid Fe(OH)₂.

Upon further exposure to air (with its supply of O_2), Fe(OH)₂ becomes Fe₂O₃.

4Fe(OH)₂ (s) + O₂ ---- 2H₂O (l) + 2Fe₂O₃ (s)

The important thing to remember in the case of my rusting car is that all three reactants (Fe, O_2 , H_2O) were present in abundance. My Nissan also had numerous warming cycles. Heat speeds up the rate of the reaction, but it also evaporates the water and exposes newly formed Fe(OH)₂ to oxygen.

Salt's Role

In addition, these reactions require a transfer medium, water. Sufficient water is necessary to transfer or conduct the electrons from the Fe anode to the O_2 cathode. But pure water is a poor conductor.

This is where salt (NaCl) comes in. NaCl breaks up into Na+ and Cl- ions in water and helps conduct electrons. The saltier a solution is, the better its conductivity. If the salt solution is warmer, say near a car's muffler or heat shield, its conductivity will also increase. The better the flow of electrons, the faster the rusting process.

The small chloride ion can also sometimes work its way past protective coatings and leach out soluble iron chloride salts, exposing new surfaces for attack.

My car was eaten by oxygen and water, but the road salt played a role too. Many of the risk factors are unavoidable, but if I can suggest one thing, it is to wash your car (especially the underside) on a regular basis to remove the road salt. I didn't, and I probably had salt aiding in the oxidation of my car long into the spring months.