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Chemical Thermodynamics of Lime Amendments

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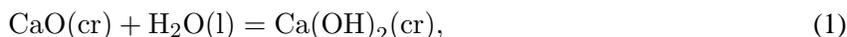
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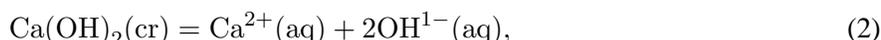
December 5, 2001

Heavy construction equipment cannot operate in many types of soils when the soils are water-saturated muds. Often soils must be dewatered to avoid delays in construction. Drying by working a chemical into the soils is a popular approach. Untrafficable muds are seasonally characteristic of most cold regions. This note presents a calculation of the effect of temperature on the pertinent chemical reactions for lime, a popular soil-drying chemical.

Wet soils can be dried by the addition of calcium oxide [CaO (cr)] or calcium hydroxide [Ca(OH)₂ (cr)]. Three reactions are considered: the hydration of calcium oxide:



the dissolution of calcium hydroxide:



and the vaporization of liquid water:



Reaction (2) increases the soil solution pH markedly, causing changes in the physical properties of the soil [Kézdi, 1979, p. 163–164]. The specific effects depend on the properties of the individual soils (their texture and mineralogy) and are not considered here further.

The standard enthalpy of reaction at 298.15 K ($\Delta_r H^\circ$) is calculated by:

$$\Delta_r H^\circ = \sum_{i=\text{products}} \nu_i \Delta_f H_i^\circ - \sum_{i=\text{reactants}} \nu_i \Delta_f H_i^\circ \quad (4)$$

where ν_i is the stoichiometric number for substance i and $\Delta_f H_i^\circ$ is its standard enthalpy of formation [Pitzer, 1995, p. 110]. At 298.15 K, $\Delta_r H^\circ$ for reaction (1) is $-65.84 \text{ kJ} \cdot \text{mol}^{-1}$ and those of reactions (2) and (3) are -7.47 and $44.004 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

$\Delta_r H^\circ$ at another temperature can be calculated by:

$$\Delta_r H_{T_f}^\circ = \Delta_r H_{T_r}^\circ + \int_{T_r}^{T_f} \Delta_r C_p^\circ dT \quad (5)$$

where $\Delta_r C_p^\circ$ is the change in the heat capacities of the system components due to the reaction [Pitzer, 1995, p. 110].

Table 1: Standard thermodynamic values for reactions resulting from lime amendments to soils [Rossini et al., 1952; Cox et al., 1989]

| Compound | M | $\Delta_f H^\circ$ (298.15 K) | S° (298.15 K) | C_p (298.15 K) |
|--------------------------|------------------------|-------------------------------|---|---|
| | kg · mol ⁻¹ | kJ · mol ⁻¹ | J · K ⁻¹ · mol ⁻¹ | J · K ⁻¹ · mol ⁻¹ |
| Ca ²⁺ (aq) | 0.0400780 | -543.0 ± 1.0 | -56.2 ± 1.0 | |
| CaO (cr) | 0.0560770 | -634.92 ± 0.90 | 38.1 ± 0.4 | 42.80 |
| Ca(OH) ₂ (cr) | 0.0740918 | -986.59 | 76.1 | 84.5 |
| H ₂ O(l) | 0.0180148 | -285.830 ± 0.040 | 69.95 ± 0.03 | 75.295 |
| H ₂ O(g) | 0.0180148 | -241.826 ± 0.040 | 188.835 ± 0.010 | |
| OH ¹⁻ (aq) | 0.0170069 | -230.015 ± 0.040 | -10.90 ± 0.20 | |

$\Delta_r C_p^\circ$ for reaction (1) is $-33.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Accordingly, for reaction (1) equation (5) becomes:

$$\Delta_r H_{T_f}^\circ = 65,840 \text{ J} \cdot \text{mol}^{-1} - 33.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}(T_f - 298.15 \text{ K}). \quad (6)$$

At 25 °C the standard enthalpy for reaction (1) decreases 0.051 % for every °C increase in temperature.

Consider a cubic meter of water-saturated soil, which contains 0.5 m³ of water and 0.5 m³ of mineral solids. If the mineral solids have densities of 2.65 Mg · m⁻³, the cubic meter of soil contains 500 kg (27,754 moles) of water and 1,325 kg of solid minerals. Assume further that CaO is added to the soil at the recommended rate of 4 % of the soil's dry weight [National Lime Association, undated]. This is 53 kg or 945 moles of CaO. Reaction (1) will remove at most 945 moles (3.4 %) of the water present in the soil.

In this scenario, reactions (1) and (2) would contribute 69,277 kJ of enthalpic energy to the soil. In principle, this energy is available to evaporate water, but certainly a significant proportion of the available energy would be dissipated by other mechanisms. If it is assumed that all of the chemical energy from reactions (1) and (2) was used only to vaporize the soil water, 1,574 moles of water (5.7 %) would be lost from the soil by this mechanism. In principle, reactions (1), (2), and (3) could reduce the amount of water in the soil as much as 9.1 %, in practice the actual amount would be less, though how much less cannot be determined from thermodynamic calculations such as these.

The addition of lime is an effective method to dry untrafficable saturated soils. Ambient temperatures have a trivial effect on the efficacy of lime amendments for this purpose.

References

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