



# MEMO

## Chemical Lime

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**To:** Bill Howard, Griffin Soil

**CC:** Tom Zaremba, Eric Berger

**Date:** 12/3/2001

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**Ref:**

**Subject:** Soil Stabilization with Lime and Storm Water Pollution Prevention Plans

### Summary:

- ❖ Properly cured and compacted lime-stabilized soils do not leach and will have minimal effects on stormwater runoff because of the soils' low permeability and high compaction.
- ❖ Uncompacted or incompletely cured lime-stabilized soils can saturate runoff waters with calcium hydroxide.
- ❖ The effects of off-site lime-water drainage will be minimized by
  - Dilution with commingled stormwaters,
  - Neutralization by formation of calcium carbonate from bicarbonate ions and carbon dioxide,
  - Neutralization by cation exchange with clays and organic trash.
- ❖ Proper construction practices and drainage control are the best means of avoiding stormwater pollution problems.

Background: A number of questions have been raised in connection with modifying Storm Water Pollution Prevention Plans (SWPPP) to address the potential for off-site effects arising from lime stabilization jobs. The following questions are addressed later in this document:

- 1) Once lime is mixed into soil and hydrated, are there any leaching effects?
- 2) If leaching does occur, is there some way to establish a dilution rate that we can somehow standardize?
- 3) If lime gets into a discharge system, what will be the effect on the system?
- 4) How can we preempt any of these concerns?
- 5) Can we actually help with erosion control by lime treatment?



Discussion of the lime stabilization process.

Lime stabilization is an ancient process which continues to be an effective construction tool through modernization and quality control. Test methods can predict the correct lime dosage<sup>1</sup> and confirm its effectiveness<sup>2</sup>. Construction techniques have been developed to broaden its applicability and versatility.<sup>3</sup> Understanding the lime stabilization process and its effects on soil and water requires delving into the chemistry.

#	Process	Reaction	Effects	Speed
1	Hydration of quicklime (calcium oxide) to calcium hydroxide.	$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$	Consumes water and releases heat. Drying action for muddy soils. Required to put lime in a form that reacts with pozzolans <sup>4</sup> .	Fairly fast Sec – Min
2	Saturation of the waters with calcium hydroxide.	$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{+2}_{\text{aq}} + \text{OH}^{-1}_{\text{aq}}$	pH increases. Calcium ion becomes mobile.	Fast Seconds
3	Saturation of ion exchange sites with calcium ions.	$\text{Ca}^{+2}_{\text{aq}} + \text{Na-clay} \leftrightarrow \text{Na}^{+1}_{\text{aq}} + \text{Ca-clay}$	<ol style="list-style-type: none"> <li>1) <math>\text{Ca}^{+2}</math> occupies cation sites.</li> <li>2) The ionic double layer thickness decreases.</li> <li>3) Water bound to clays is released from the double layers.</li> <li>4) Clays coagulate and flocculate.</li> </ol>	Fast Seconds

<sup>1</sup> ASTM C 977-95, Standard Specification for Quicklime and Hydrated Lime for Soil Stabilization, ASTM D 6276-99a - Standard Test Method for Using pH to Estimate the Soil-Lime Proportion Requirement for Soil Stabilization

<sup>2</sup> ASTM D 3877-96 - Standard Test Methods for One-Dimensional Expansion, Shrinkage, and Uplift Pressure of Soil-Lime Mixtures, ASTM D 5102-96 - Standard Test Method for Unconfined Compressive Strength of Compacted Soil-Lime Mixtures, ASTM D 6276-99a - Standard Test Method for Using pH to Estimate the Soil-Lime Proportion Requirement for Soil Stabilization

<sup>3</sup> Little, Dallas N., 1995, Handbook for Stabilization of Pavement Subgrades and Base Courses with Lime, NLA sponsor, 219 pages.

<sup>4</sup> **Pozzolan** - “Finely divided siliceous or siliceous and aluminous material that reacts chemically with slaked lime (calcium hydroxide ) at ordinary temperature and in the presence of moisture to form a strong slow-hardening cement”, [*Italian pozzolana (1706)*], Webster’s New Ninth Collegiate Dictionary, 1983, p. 923. Pozzolans include many clay minerals, Fly ash, finely divided silica, volcanic ashes, natural and synthetic siliceous glasses.



Table 1: The Chemical Stages of Lime Stabilization of Soils				
#	Process	Reaction	Effects	Speed
			5) The physical properties of clay minerals change.	
4	Alkaline attack on silicate minerals.	$\text{SiO}_2 + \text{H}_2\text{O} + \text{OH}^{-1}_{\text{aq}} \leftrightarrow \text{H}_3\text{SiO}_4^{-1}_{\text{aq}}$	Strong function of pH. See chart 1 below. $\text{pH} \geq 11.5$	Moderate Min – Hrs
5	Alkaline attack on aluminous minerals to form aluminate ion.	$\text{Al}^{+3}\text{-mineral} + 4\text{OH}^{-1}_{\text{aq}} \leftrightarrow \text{Al}(\text{OH})_4^{-1}_{\text{aq}}$	Strong function of pH. See chart 2 below. $\text{pH} \geq 11.5$	Moderate Min – Hrs
6	Polymerization of silica-complexes <sup>5</sup> , for example: $\Rightarrow$	$\text{Si}_3\text{O}_5(\text{OH})_5^{-3}$ , $\text{Si}_4\text{O}_6(\text{OH})_6^{-2}$ , etc.	Preparation for colloid and gel formation preparatory to new mineral precipitation.	Moderately fast ? Minutes
7	Formation of hydrous calcium alumino-silicate colloids & gel as pH stabilizes or drops due to hydroxyl consumption, for example:	$\text{H}_3\text{SiO}_4^{-1}_{\text{aq}} + \text{Al}(\text{OH})_4^{-1}_{\text{aq}} \leftrightarrow \text{AlSiO}_2(\text{OH})_5^{-2} + \text{H}_2\text{O}$ $x \text{Ca}^{+2}_{\text{aq}} + \text{AlSiO}_2(\text{OH})_5^{-2} \leftrightarrow (\text{Ca}_x\text{AlSiO}_2(\text{OH})_5)^{-2+2x}$	Presumably pore filling CSH-like materials.	Moderately slow Hrs – Days
8	Formation of hydrous calcium-aluminosilicate minerals, for example:	Chabazite, $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ ; Tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$	Strength development	Slow Days – Weeks

The steps<sup>6</sup> of an on-site lime stabilization operation are:

- 1) Bring the site to final grade.
- 2) Apply lime in the prescribed dosage. Lime may be applied as dry quicklime, dry hydrate, or lime slurry.
- 3) Add sufficient water to take the limed soil mixture above the optimum moisture level of the limed soil. This optimum moisture level will generally be higher than the untreated soil due to clay flocculation.
- 4) Mix the lime, soil, water to the target depth, breaking clay clods down to <25 mm (1 inch) with the majority <5 mm (4 mesh) size.

<sup>5</sup> Andrew R. Felmy, Herman Cho, David A. Dixon, James R. Rustad, Zheming Wang, and Gregory R. Choppin, 2000, The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface, <http://www.pnl.gov/emsp/fy2002/presentations/index.html>

<sup>6</sup> Little, 1995, pages 164-177, 179-183.



- a) Multiple mixing passes and depths may be needed.
  - b) Some projects will require mellowing periods to allow the stabilization processes to break down clay masses, exposing fresh clay to lime treatment by additional mixing. Maintain moisture levels above the optimum through the mellowing period.
  - c) Especially heavy clays or refractory soils may require additional lime applications, water and mixing to fully break up and treat the soil masses.
  - d) If mellowing or multiple treatments are required, the treated soils should be lightly rolled or sealed to control moisture flux.
- 5) As soon as feasible, compact the treated mixture to the specified density (commonly 95% of maximum density). Maintain the moisture level at or slightly above optimum. Prompt compaction minimizes moisture loss and recarbonation of the calcium hydroxide.
  - 6) A curing period after compaction and before paving or construction allows additional strength and durability development.

In addition to pozzolanic reactions, lime undergoes many other important reactions affecting its environmental impact:

<b>Table 2: Environmental Lime Reactions</b>		
Reaction Name	Equation	Consequences
Hydration	$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{Heat}$	Converts quicklime, CaO, to calcium hydroxide with release of heat.
Recarbonation	$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	Carbon dioxide from the air converts lime to calcium carbonate (limestone) and lowers the pH
Water Softening – calcium removal	$\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2 \text{CaCO}_3 + 2 \text{H}_2\text{O}$	Removes calcium from hard water. Neutralizes bicarbonate ion and consumes hydroxide. (pH ≥ ~8-9)
Water Softening – magnesium removal	$\text{Mg(HCO}_3)_2 + 2 \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 + 2 \text{CaCO}_3 + 2 \text{H}_2\text{O}$	Removes magnesium and hydroxide as precipitate. Neutralizes bicarbonate ion and consumes hydroxide. (pH ≥ ~9)
Ion Exchange	$\text{Ca}^{+2}_{\text{aq}} + \text{Na-clay} \leftrightarrow \text{Na}^{+1}_{\text{aq}} + \text{Ca-clay}$	Flocculates clays to larger particles, reducing Total Suspended Solids (TSS), and clarifying water.



Questions concerning environmental effects:

1) **Once lime is mixed into soil and hydrated, are there any leaching effects?**

- a) Leaching is not normally a problem in a job where the compaction proceeds directly after mixing. The permeability of lime-stabilized soils approaches that of compacted clay liners required of landfills and hazardous waste enclosures.

<b>Table 3: Permeability of Selected Soil Materials</b>		
Material	Hydraulic conductivity or Permeability, centimeters/second	Comments
Landfill liner of compacted soil layer	1E(-7) cm/s	Maximum permitted by law <sup>7</sup>
Lime-stabilized clay <sup>8</sup>	Smectitic – 0% lime addition – 7.81 E(-10) cm/s, 4% lime addition – 4.93 E(-7) cm/s, 7% lime addition – 1.14 E(-8) cm/s, 9% lime addition – 4.52 E(-8) cm/s	Hydraulic conductivity values
Lime-stabilized silty clay <sup>9</sup>	Illitic – 0% lime addition – 9.31 E(-10) cm/s, 4% lime addition – 1.71 E(-7) cm/s, 7% lime addition – 6.35 E(-7) cm/s, 9% lime addition – 1.12 E(-6) cm/s	Hydraulic conductivity values
Lime-stabilized silty clay loam <sup>10</sup>	Kaolinitic – 0% lime addition – 7.15 E(-8) cm/s, 4% lime addition – 6.77 E(-7) cm/s, 7% lime addition – 1.20 E(-6) cm/s, 9% lime addition – 4.24 E(-6) cm/s	Hydraulic conductivity values

<sup>7</sup> 40 CFR 258.40 (b)<sup>7</sup>, <http://www.epa.gov/docs/epacfr40/chapt-I.info/subch-I.htmf>

<sup>8</sup> 5837, Omidi, G.H., Prasad, T.V., Thomas, J.C. & Brown, K.W., 1996, The Influence of Amendments on the Volumetric Shrinkage and Integrity of Compacted Clay Soils Used in Landfill Liners, Water, Air and Soil Pollution, Vol. 86, pp. 263 - 274

<sup>9</sup> 5837, Omidi, G.H., Prasad, T.V., Thomas, J.C. & Brown, K.W., 1996, The Influence of Amendments on the Volumetric Shrinkage and Integrity of Compacted Clay Soils Used in Landfill Liners, Water, Air and Soil Pollution, Vol. 86, pp. 263 - 274



A study<sup>11</sup> of leaching of lime-stabilized soils concluded:

“...Maximum detrimental changes generally occurred at lime contents at or less than the lime modification optimum. At lime contents at or above the lime stabilization optimum, the detrimental effects of leaching were minimized or eliminated...” (after 600 hours leaching by distilled water at 10 psi). At high ( $\geq 6\%$ ) lime addition for heavy montmorillonitic clays, the Plasticity Index (PI) remained the same or decreased after 45 days leaching, indicating the soil stabilization effects are permanent. The unconfined compressive strength at these lime addition rates actually increased with time of leaching.

The permanent nature of the stabilization reaction indicates the reaction is not reversible and the calcium hydroxide has transformed into a low solubility hydrous calcium aluminosilicate compounds just as portland cement changes in the curing of concrete.

- b) If a rain event occurs before compaction, deeper penetration of the water occurs and more high pH soil is contacted. This increases the amount of lime that can be dissolved. We can estimate the amount of water that contacts uncompacted, high pH material and the amount of lime that might be dissolved. The simplest worst case considers the uncompacted soil as a pass-through reactor in which lime is released to the water passing through. This might be the case of a porous, uncompacted, stabilized soil on a slope.

The amount of lime available to dissolve in rainwater is a function the lime dosage, the depth of the “leaching zone”, and the degree of lime reactions consuming  $\text{Ca}(\text{OH})_2$ . Figure 3 (at end) reflects the greater amounts of lime leachable from higher dosage, thicker sections, more rainfall and higher unreacted lime. While the low solubility of lime ( $\sim 1.5 \text{ g Ca}(\text{OH})_2/\text{L} \sim 0.02 \text{ M/L}$ ) means that rainwater is readily saturated by a small amount of lime, it also means that the dissolved lime is readily neutralized or consumed by common environmental reactions.

- c) In reality, the amount of lime-saturated water that could leave the site is fairly low. The soil would have a certain pore volume which would fill with water. A soil porosity of 30% would permit water imbibition equal to  $\sim 1/3$  the depth of disturbance.

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<sup>10</sup> 5837, Omidi, G.H., Prasad, T.V., Thomas, J.C. & Brown, K.W., 1996, The Influence of Amendments on the Volumetric Shrinkage and Integrity of Compacted Clay Soils Used in Landfill Liners, Water, Air and Soil Pollution, Vol. 86, pp. 263 - 274

<sup>11</sup> McCallister, Larry D. and Petry, Thomas M., 1991, Physical Property Changes in a Lime Treated Expansive Clay Caused by Leaching (TRB, 1991), Transportation Research Record #1295, pp 37-44.



The imbibed water would become saturated, but not expelled. Excess surface water would contact the surface layers, but not pass through or penetrate so as to become fully lime-saturated. The excess surface water would only be affected to the extent that mixing processes brought saturated lime water out of the soil layer or eroded and entrained loose limed materials.

**2) If leaching does occur, is there some way to establish a dilution rate that we can somehow standardize?**

Dilution effects: Saturated lime water has a pH of 12.4. Each 10-fold dilution with pure water reduces the pH by one unit. The upper limit for many discharge permits is generally 9.0 or 9.5. A straight 1000-fold dilution would reduce the pH of a saturated lime achieves water from ~12.4 to ~9.4. The dilution rate could be estimated made by the ratio of the drainage areas of the untreated areas draining to lime treated area to the same system, assuming the same runoff rate. Dilution ratio ~  $\frac{\text{(Area of untreated drainage)}}{\text{(Area of lime-treated drainage)}}$

Cation exchange effects: The dilution ratio neglects the buffer capacity of runoff waters to decrease the pH of lime-bearing water. Mixing clay-containing waters from untreated soils with water containing dissolved lime with can reduce the turbidity and the pH effect of the lime to a minor degree.

The suspended clay solids have a Cation Exchange Capacity (CEC) that can remove and neutralize some calcium hydroxide, depending on the exchangeable site occupancy. Assuming a muddy water TSS of 40 mg/L<sup>12</sup> consists of clay with a CEC of 200 meq/kg, we can make an estimate of the calcium hydroxide that can be consumed.

TSS cation capacity:  $40 \text{ mg/L} \times 200 \text{ meq/kg} \times 10^{-6} \text{ mg/kg} = 8 \times 10^{-3} \text{ meq/L}$

Lime solubility:  $(1.5 \text{ g/L} \times 2 \text{ eq/mole} \times 1000 \text{ meq/eq}) / 74.09 \text{ g/mole} = 40.5 \text{ meq/L}$

Lime solubility/TSS cation capacity =  $40.5/0.008 = 5062$

[There is generally no limit specified for Total Suspended Solids (TSS), although Colorado regulations are typical in stating: "Suspended solid levels will be controlled by Effluent Limitation Regulations,

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<sup>12</sup> Three WA streams had average TSS values of 4, 6, and 20 with peak values of 6, 9, and 44, respectively. <http://www.ecy.wa.gov/programs/wq/plants/management/joysmanual/streamtss.html>



Basic Standards, and Best Management Practices (BMP's).<sup>13</sup> High TSS levels impair biological activity and water quality.<sup>14</sup>]

### **3) If lime gets into a discharge system, what will be the effect on the system?**

Drainage to sewage system: Lime is a coagulant and flocculating agent used in many sewage treatment processes. The calcium is assimilated by the microflora. The buffering capacity of the wastewater is generally sufficient to moderate the pH. A number of wastewater treatment plants use pre-lime stabilization to coagulate sewage. The lime water from the dewatering stage is directed back to the headworks without ill effect on the biological process. The volume of recycled lime water is very small compared to influent volume.

Drainage to stormwater system: Lime is a treatment chemical used in potable water systems in the first stage of a standard coagulation, flocculation, and sedimentation system. Dilution in the stormwater system will reduce the pH. Decomposing organic trash (leaves, plant trash, etc.) has a high cation exchange capacity and is generally rich in organic acids.

Suspended clays in the commingled stormwater will be flocculated by ion exchange. These will promptly settle out, reducing the turbidity.

### **4) How can we preempt any of these concerns?**

Good construction practices and timely execution of projects will preempt these effects. On-site drainage control is required in most jurisdictions. Local runoff impoundment, silt fences, and working with an eye to weather forecasts are standard precautions.

For moderate rainfall events, permitting the water to soak into the uncompacted stabilized soil is advantageous. The stabilization reactions consume water and are accelerated by maintenance of high pH conditions.

### **5) Can we actually help with erosion control by lime treatment?**

Lime treatment converts clay materials to a strong, less erodible material. Thoroughly cured stabilized soils are hard and strong. The sand equivalent of a soil material increases almost instantly upon addition of lime. Small amounts of surface splash or overwash to adjacent unlimed soils will cause ion exchange and flocculation of the clays, reducing the erodability.

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<sup>13</sup> <http://www.cdph.state.co.us/op/regs/100231.pdf>

<sup>14</sup> The National Academy of Sciences has recommended that the concentration of TSS should not reduce light penetration by more than 10%. In a study in which TSS were increased to 80 mg/L, the macroinvertebrate population was decreased by 60%.



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