

LEACHING & STORM WATER RUNOFF

LEACHING AND STORM WATER CONCERNS – The following questions address the issues of chemically stabilized soils and aggregates on projects where a Storm Water Pollution Protection Program (SWPPP) is implemented:

1. Once stabilizing reagent is mixed into a soil and/or aggregate and hydrated, are there any leaching effects?
2. If leaching does occur, is there some way to establish a dilution rate that can be standardized?
3. If reagent 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 chemically stabilizing soil?

A properly designed and constructed chemically stabilized soil and/or aggregate section will not leach or have a detrimental effect on Storm Water runoff. If the treated section is correctly hydrated, compacted, and cured, the result will be a section with a relatively low permeability and high surface durability.

If a chemically treated soil and/or aggregate are left un-compacted or incompletely cured, the results can lead to saturating runoff waters with calcium hydroxide. The following will minimize the effects of calcium hydroxide into storm water systems:

- Dilution with combined storm waters,
- Neutralization by formation of calcium carbonate from bicarbonate ions and carbon dioxide,
- Neutralization by cation exchange with clays and/or organic trash.

Proper construction practices and drainage control are the best practice means of avoiding storm water pollution problems and/or leaching.

BACKGROUND - Chemical (Cementitious) stabilization is an ancient process, which continues to grow as an effective design and construction tool through modernization and quality control. Test methods can predict the correct stabilizer dosage¹ and confirm its effectiveness². Design and construction techniques

¹ 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

² 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

have been developed to broaden its applicability and versatility³ in various engineering applications, including; pavements, water resource, and environmental remediation.

Understanding the chemical stabilization process and its effects on soil and water requires delving into the chemistry:

**TABLE 1
THE STAGES OF CHEMICAL STABILIZATION**

	PROCESS	REACTION	EFFECTS	TIME
1	Hydration - (calcium oxide) to calcium hydroxide.	$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$	Consumes water and releases heat. Drying action for muddy soils. Required for CaO to react with pozzolans ⁴ .	Fairly fast Sec – Min
2	Saturation of the waters with calcium hydroxide.	$\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{+2}_{\text{aq}} + \text{OH}^-$	pH increases. Calcium ion becomes mobile.	Fast Seconds
3	Saturation of ion exchange with calcium ions.	$\text{Ca}^{+2}_{\text{aq}} + \text{Na-clay} \leftrightarrow \text{Na}^{+1}_{\text{aq}} + \text{Ca-clay}$	1) Ca^{+2} occupies cation sites. 2) The ionic double layer thickness decreases. 3) Water bound to clays is released from the double layers. 4) Clays coagulate and flocculate. 5) The physical properties of clay minerals change.	Fast Seconds
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

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

⁴ **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.

	PROCESS	REACTION	EFFECTS	TIME
5	Alkaline attack on aluminous minerals to form aluminate ion.	$Al^{+3}\text{-mineral} + 4OH^{-1}_{aq} \leftrightarrow Al(OH)_4^{-1}_{aq}$	Strong function of pH. See chart 2 below. $pH \geq 11.5$	Moderate Min – Hrs
6	Polymerization of silica-complexes ¹ , for example: \Rightarrow	$Si_3O_5(OH)_5^{-3}$, $Si_4O_6(OH)_6^{-2}$, etc.	Preparation for colloid and gel formation preparatory to new mineral precipitation.	Moderately fast? Minutes
7	Formation of hydrous calcium aluminosilicate colloids & gel as pH stabilizes or drops due to hydroxyl consumption, for example:	$H_3SiO_4^{-1}_{aq} + Al(OH)_4^{-1}_{aq} \leftrightarrow AlSiO_2(OH)_5^{-2} + H_2O$ $x Ca^{+2}_{aq} + AlSiO_2(OH)_5^{-2} \leftrightarrow (Ca_xAlSiO_2(OH)_5)^{-2+2x}$	Presumably pore filling CSH-like materials.	Moderately slow Hrs – Days
8	Formation of hydrous calcium-aluminosilicate minerals, for example:	Chabazite, $CaAl_2Si_4O_{12} \cdot 6H_2O$; Tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4(H_2O)$	Strength development	Slow Days – Weeks

¹ 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>

STEPS OF A PROPERLY STABILIZED SECTION

- 1) Bring the site to the required treatment grade.
- 2) Apply chemical reagent to a prescribed dosage. Reagent applied as dry powder.
- 3) Add sufficient water to take the treated soil mixture above the optimum moisture level, with enough water for hydration of reagent. This optimum moisture level will generally be higher than the untreated soil due to soil flocculation.
- 4) Mix the reagent, soil, and water to the design depth.
 - a) Multiple mixing passes and depths may be needed to breakdown clods to <25 mm (1 inch) with the majority <5 mm (#4 mesh) size.

- b) Some projects will require an extended mellowing period to allow for the stabilization processes to break down clay clods. Maintain moisture levels above the optimum through the mellowing period.
 - c) Especially heavy clays or refractory soils may require additional 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 re-carbonation 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, cementitious reagents undergoes many other important reactions affecting its environmental impact:

**Table 2
Environmental Calcium Oxide (CaO) Reactions**

Reaction Name	Equation	Consequences
Hydration	$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{Heat}$	Converts CaO, to calcium hydroxide with release of heat.
Re-carbonation	$\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	Carbon dioxide from the air converts CaO to calcium carbonate (limestone) and lowers the pH
Water Softening – calcium removal	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2 \text{CaCO}_3 + 2 \text{H}_2\text{O}$	Removes calcium from hard water. Neutralizes bicarbonate ion and consumes hydroxide. (pH ≥ ~8-9)
Water Softening – magnesium removal	$\text{Mg}(\text{HCO}_3)_2 + 2 \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + 2 \text{CaCO}_3 + 2 \text{H}_2\text{O}$	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 reagent 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 stabilized soils approaches that of compacted clay liners required of landfills and hazardous waste enclosures.

**Table 3
Permeability of Selected Soil Materials**

Material	Hydraulic conductivity or Permeability, centimeters/second	Comments
Landfill liner of compacted soil layer	1E(-7) cm/s	Maximum permitted by law ⁵
Lime-stabilized clay⁶	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/Cement-stabilized silty clay⁷	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/Cement-stabilized silty clay loam⁸	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

⁵ 40 CFR 258.40 (b)⁵, <http://www.epa.gov/docs/epacr40/chapt-I.info/subch-I.htmf>

⁶ 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

⁷ 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

⁸ 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 RECENT LEACHING STUDY₉ OF STABILIZED SOIL:

“...Maximum detrimental changes generally occurred at reagent contents at or less than the reagent modification optimum. At reagent contents at or above the lime or cement 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 higher pH soil is contacted. This increases the amount of reagent that can be dissolved. We can estimate the amount of water that contacts un-compacted, high pH material and the amount of reagent that might be dissolved. The simplest worst case considers the un-compacted soil as a pass-through reactor in which CaO is released to the water passing through. This might be the case of a porous, un-compacted, stabilized soil on a slope.

The amount of reagent available to dissolve in rainwater is a function the reagent dosage, the depth of the “leaching zone”, and the degree of reagent reactions consuming Ca (OH)₂. Figure 3 (at end) reflects the greater amounts of reagent leachable from higher dosage, thicker sections, more rainfall and higher un-reacted reagent. While the low solubility of lime (~ 1.5 g Ca (OH)₂/L ~ 0.02 M/L) means that rainwater is readily saturated by a small amount of reagent, it also means that the dissolved CaO is readily neutralized or consumed by common environmental reactions.

- c) In reality, the amount of CaO-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 imbibitions equal to $\sim 1/3$ the depth of disturbance. 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 limewater 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: A saturated limewater 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 or cement 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 stabilized area to the same system, assuming the same runoff rate.

Cation exchange effects: The dilution ratio neglects the buffer capacity of runoff waters to decrease the pH of lime or cement-bearing water. Mixing clay-containing waters from untreated soils with water containing dissolved lime or cement can reduce the turbidity and the pH effect of the lime or cement 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 muddy water TSS of 40 mg/L⁹ 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 and cement 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, Basic Standards, and Best Management Practices (BMP's)."¹⁰ High TSS levels impair biological activity and water quality.¹¹]

⁹ 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>

¹⁰ <http://www.cdphe.state.co.us/op/regs/100231.pdf>

¹¹ 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%.

3) If lime or cement 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 micro flora assimilates the calcium. 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 limewater from the dewatering stage is directed back to the headwork's without ill effect on the biological process. The volume of recycled limewater is very small compared to influent volume.

Drainage to storm water 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 storm water 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 storm water 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 un-compacted 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 or cement treatment?

Chemical treatment converts soils and aggregates to a strong, less erodible material. Thoroughly cured stabilized soils or aggregates are hard and strong. The sand equivalent of a soil material increases almost instantly upon addition of reagent. Small amounts of surface splash or over-wash to adjacent un-limed soils will cause ion exchange and flocculation of the clays, reducing those reducing its erodability.

For moderate rainfall events, permitting the water to soak into the un-compacted stabilized soil is advantageous. The stabilization reactions

consume water and are accelerated by maintenance of high pH conditions.

**TABLE 4
ESTIMATION OF EFFECTS OF RAINFALL LEACHING**

Rainwater, saturated with carbon dioxide, will neutralize some dissolved lime. Assumptions: 1) 50% of lime has reacted in stabilization reaction.2) Depth of leaching, rainfall amount.		
Parameter	Molar Concentration	Equivalents Concentration
Initial Project Conditions	Lime Stabilization Dosage = 6%	Lime Available for Reaction = 50%
Amount of Lime Available for Leaching	8.24E-04 moles/sq.cm.	1.65E-03 Equivalents/sq.cm.
Rainfall Effects	Rainfall = 3"	Leaching Depth = 0.5 inch
Lime that can be dissolved in pure water	2.66E-06 moles/sq.cm.	5.31E-06 Equivalents/sq.cm.
Neutralizing and reacting capacity for the rainfall volume:	1.10E-07 moles/sq.cm. Carbonic acid → Bicarbonate ion	1.87E-07 Equivalents/sq.cm.
Ratios (Equivalents):	Lime Available: Dissolving Power = 300 X	Lime Available: Neutralizing Capacity = 8800 X
	Dissolving Power: Neutralizing Capacity = 28 X	

*** In this document the use of the word Reagent refers to only High Calcium Quicklime, Dolomitic Quicklime, and Portland cement Type II to V. It is important to note that Portland cement is comprised on 60 to 65 percent CaO (Quicklime). Both Quicklime and Portland cement provide the same cementitious performance and the choice of one reagent over the other is a function of the soil characteristics'.**