# Can Phosphate Be Used To Improve The Hazardous Status Of High Density Sludge And Transform It Into An Agricultural Product?

B.H. Sukati, P.C. De Jager, J.G. Annandale, P.D. Tanner

*Department of Plant and Soil Sciences, University of Pretoria, X20, Hatfield 0028, South Africa*
*chris.dejager@up.ac.za*

## Abstract

High Density Sludge (HDS) is often classified as hazardous due to metal solubility. The objective was to investigate if phosphate ($PO_4$) treatment can stabilize HDS. HDS with high soluble Mn (Hi-sol Mn) and another with low soluble Mn (Lo-sol Mn) were treated with 50 mg/L P and 4000 mg/L P solutions. Lo-sol Mn showed low metal solubility before and after treatment. Soluble Ni in Hi-sol Mn was reduced from 2.9 to 0.07 mg/L after 4000 mg/L P treatment and Pb remained at <0.1 mg/L before and after treatment. This improved both materials towards a better plant nutrient source.

**Keywords:** High Density Sludge, TCLP, AMD

## Introduction

High density sludge (HDS) is generated during acid mine drainage (AMD) treatment by a mixture of recycled sludge and a combination of limestone ($CaCO_3$) and lime ($Ca(OH)_2$) (Aubé and Zinck 1999). Depending on the chemical used to treat AMD, HDS can be alkaline regardless of the process and contains varying concentration of various transition metals (e.g Ni, Pb, Hg, Co, Cr, Cd, Zn, Cu). These metals can be traced back to the chemistry of AMD treated and the liming material (Johnson and Hallber 2005, Kalin et al. 2006). Based on composition and solubility of metals, HDS is often classified as a hazardous waste. The potential environmental risk is a function of the solubility of these metals.

From an agricultural point of view, it contains various elements essential for plant growth. As a result of the treatment, it is particularly high in Ca and S, as $SO_4$, residing in gypsum ($CaSO_4.2H_2O$). Other essential elements are Mg, an element often deficient in highly leached soils, and trace elements like Zn and Cu. The material also contains 10 – 30 % residual lime depending on the process (Maree et al. 2004 and Zinck 2006) that can increase the pH of acid soils. Using phosphate ($PO_4$) to chemically stabilize waste by decreasing the solubility of metals in it, is a well-established practice. Metal stabilization by $PO_4$ was demonstrated; in bottom ash of municipal solid wastes (Crannell et al. 2000), in polymineralic mine wastes (Harris and Lottermoser 2006), and in soils (Kumpiene et al. 2006). Phosphate facilitates surface sorption and precipitation of especially transition metals reducing their solubility. Crannell et al. (2000) results indicated that Pb was precipitated by $PO_4$ into a sparingly soluble mineral, lead hydroxypyromorphite ($Pb_5(PO_4)_3OH$). According to Barthel and Edwards (2004), Kumpiene at al. (2008) metal-phosphate precipitates have low solubility due to their low $K_{sp}$ (solubility potential) values. Stabilization of other metals (e.g. Zn, Cu, Cd) also occurs on the surfaces of $Ca_5(PO_4)_3OH$ through sorption processes or by isomorphous substituting for Ca in the $Ca_5(PO_4)_3OH$ structure (Eighmy et al. 1997 and Crannell et al. 2000). Not investigated in these studies were the potential redox stabilisation introduced by phosphate. HDS contains a fair amount of iron oxides, hence the objective of this study, was to investigate the effectiveness of phosphate ($PO_4$) as a form of environmental stabilisation of metals in HDS. That is if phosphating decreases the susceptibility of HDS to reduction and if this decreases the solubility of the constituents of HDS, for example metals, such as Ni and Pb.

## Methods

### *Types of HDS used and their sources*

Two HDS sludges from Mpumalanga Coalfields in South Africa, sampled in 2016, were considered. One HDS was sourced from an AMD treatment plant that uses $CaCO_3$ alone (Hi-Sol Mn HDS). The other was from a plant that uses a combination of $CaCO_3$ and $Ca(OH)_2$ (Lo-Sol Mn HDS).

### *Determination of mineralogy*

Mineralogy of HDS was determined with X-ray Diffraction (XRD) before and after phosphating. PANalytical X'Pert Pro Powder Diffractometer. The procedure described by Loubser and Verryn (2008) was followed.

### *Alkalinity and pH determination*

The pH was determined before and after phosphating as described by Thomas (1996) in Methods of Soil Analysis Part 3 Chemical Methods (1996) in both HDS types.

### *Phosphating of HDS and solubility assessment*

The two types of HDS were treated with solutions spanning a wide phosphate concentration range: 0, 50, 100, 250, 500, 1000, 2000, 4000 and 6000 mg P $l^{-1}$. In each case, one gram of material was reacted with 25 ml of solution prepared from $KH_2PO_4$. Equilibration was allowed to occur for two days at constant temperature (25 °C). During this time the stoppered tubes were shaken end to end at 180 oscillations per minute for 2 hours per day. After 48 hours the samples were centrifuged at 300 revolutions per minute for 10 minutes and filtered through Whatman No. 42 filter paper and 0.45 µm EconoClear membrane filters. Standard P solutions; 0, 5, 10, 50, 100 1nd 250 mg $l^{-1}$ were prepared and read through ICP-OES before the determination of P in the filtered solutions. This data as used separately to asses P sorption of HDS. The phosphated material was then oven-dried at 30 °C until attained a constant mass. To assess metal solubility before and after phosphating the Toxicity Characteristic Leaching Procedure (TCLP 1311): from the Solid Waste Manual 846 (SW-846) by the US Environmental Protection Agency (EPA) (1992) was used.

### *Determination of total elemental content before and after phosphating*

Microwave assisted acid digestion, EPA method 3052 (EPA SW-846 2014) was followed. After digestion, elements were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES. X-ray Fluorescence (XRF) which uses ARL 9400XP+ Wavelength dispersive XRF Spectrometer was also used to determine total elemental content following the procedure described by Loubser and Verryn (2008).

### *Redox stability assessments*

Susceptibility to reductive dissolution was investigated by using reductants to extract Fe, Mn, Al, Pb and Ni. As discussed by Courchesne and Turmel (2007), dithionite-citrate, was used to determine amorphous inorganic forms of Al, Fe and Mn. Similarly, acid ammonium oxalate and acid hydroxylamine were also used to estimate the same elements and forms as with dithionite-citrate, but to a lesser extent crystalline form.

### *Determination of Total Electron Demand (TED) and Manganese Electron Demand (MED) before and after phosphating*

Total Electron Demand and MED were determined by following procedures described by Bartlett and James (1995).

## Results and discussion

### *Mineralogy and basic chemical properties of non-phosphate HDS*

The pH of Hi-Sol Mn HDS was 5.5 with an alkalinity of 13 while Lo-Sol Mn HDS had a pH of 8.2 with an alkalinity of 16 as $CaCO_3$ (Table 1). The acidic pH in Hi-Sol Mn HDS was due to the use of $CaCO_3$ alone which has slow reaction kinetics and there was possibility of particles being coated by Fe precipitates making it unable to achieve a higher pH (Lottermoser 2007). While the alkaline pH 8.2 of Lo-Sol Mn HDS resulted from using the combination of $CaCO_3/Ca(OH)_2$. Limestone effectively increases the solution pH to 4.5 and from this point $Ca(OH)_2$ is used to increase the pH to desired levels precipitating most metals (Wilmoth 1977 and Lottermoser 2007).

*Table 1: Mineralogy and basic chemical properties of HDS*

| Parameter | | Hi-Sol Mn HDS | Lo-Sol Mn HDS | Units |
|---|---|---|---|---|
| Process | | Limestone | Lime/Limestone | |
| $pH_{H2O}$ | | 5.5 | 8.2 | |
| Total Alkalinity as $CaCO_3$ | | 13 | 16 | mg $kg^{-1}$ |
| Mineralogy [a] | | Gypsum (72 – 77 %), 22 % ferric hydroxide ($Fe(OH)_3$, 4 % ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) | Gypsum (> 95 %) | |
| Total elemental content [b] | As | 0.1 | 0.5 | mg $kg^{-1}$ |
| | B | 379.7 | 329 | mg $kg^{-1}$ |
| | Ba | 465 | 118 | mg $kg^{-1}$ |
| | Cd | < 1 | <0.1 | mg $kg^{-1}$ |
| | Ca | 182961 | 235849 | mg $kg^{-1}$ |
| | Co | 73 | 149 | mg $kg^{-1}$ |
| | Cu | 80 | 15.5 | mg $kg^{-1}$ |
| | Cr | 68 | 134 | mg $kg^{-1}$ |
| | Fe | 146319 | 114570 | mg $kg^{-1}$ |
| | Hg | N.A. | <0.1 | mg $kg^{-1}$ |
| | Mg | 6513 | 46015 | mg $kg^{-1}$ |
| | Mn | 7590 | 7847 | mg $kg^{-1}$ |
| | Mo | 3.3 | 2.8 | mg $kg^{-1}$ |
| | Ni | 108 | 167 | mg $kg^{-1}$ |
| | Pb | <1 | 143 | mg $kg^{-1}$ |
| | Sb | N.A. | N.A. | mg $kg^{-1}$ |
| | Se | 25 | 21 | mg $kg^{-1}$ |
| | V | 56 | 4 | mg $kg^{-1}$ |
| | Zn | 285 | 611 | mg $kg^{-1}$ |

[a] Determined by XRD, [b] Determined by XRF

Hi-Sol Mn HDS was approximately 72 – 77 % crystalline phase of $CaSO_4.2H_2O$ (Table 1). According to Zinck et al. (1997), Aubé and Lee (2015) the only mineral often identified in fresh HDS are $CaSO_4.2H_2O$ and $CaCO_3$. Gypsum precipitation in sludge was facilitated by high concentrations of Ca from the limestone and S from AMD. In addition XRD further showed 4 % of a carbonate mineral – ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$). Ankerite formation was facilitated by the lower pH (5.5) of HDS and the increased concentrations of Fe, Mg, Mn and Ca (Hendry et al. 2000 and Lollar et al. 2005). Amorphous $Fe(OH)_3$ formed 22 % of the non-phosphated Hi-Sol Mn HDS mineral composition. XRD technique showed > 95 % crystalline phase of $CaSO_4.2H_2O$ as the only mineral that was dominating the non-phosphated Lo-Sol Mn HDS (Table 1).

## *Phosphate effect on the reduction of Hi-Sol Mn and Lo-Sol Mn HDS*

The main environmental concern was the solubility of metals requiring chemical stabilization, especially Pb and Ni in HDS (Table 2). The solubility of these metals is controlled by pH and the addition of $PO_4$ at 4000 mg P $l^{-1}$ slightly reduced the pH by 0.6 down to 4.9 for the Hi-Sol Mn HDS. Phosphating effectively prevented the reduction of Hi-Sol Mn HDS which further reduced Ni solubility. Soluble Ni (2.9 mg $l^{-1}$) in the non-phosphated material was reduced by a maximum of 97.6 %. The reduction in soluble Ni substantially improved the environmental hazardous status of Hi-Sol Mn HDS. Solubilities of other metals including Pb were extremely low even before the addition of $PO_4$, that is, in the non-phosphated Hi-Sol Mn HDS. To further explain

***Table 2:** total and leachable concentrations of constituents for both HDS*

| Constituents | Hi-Sol Mn HDS | | | | | | Lo-Sol Mn HDS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Non-phosphated | | Phosphated at 50 mg P kg-1 | | Phosphated at 4000 mg P kg-1 | | Non-phosphated | | Phosphated at 50 mg P kg$^{-1}$ | | Phosphated at 4000 mg P kg$^{-1}$ | |
| | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) | TC (mg kg$^{-1}$) | TCLP (mg l$^{-1}$) |
| Fe | 146319 | <0.01 | 149158 | 1.9 | 142353 | 0.02 | 114570 | <0.4 | 114940 | 0.14 | 94947 | <0.01 |
| Mn | 7590 | 259 | 6016 | 4.8 | 5207 | 1.16 | 7847 | <0.04 | 7772 | 2.9 | 6867 | 1.03 |
| Ni | 108 | 2.9 | 107.5 | 0.26 | 104.7 | 0.07 | 167.3 | <0.04 | 159.5 | 0.26 | 128.6 | <0.01 |
| Pb | <1 | <0.1 | <1 | <0.1 | <1 | <0.1 | 143 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |

Note: TC = Total Concentration; TCLP = Toxicity Characteristic Leaching Procedure, N.A. = Not analysed, N.R. = Not Reported

elemental speciation and mineral phases formed, Phreeqc Interactive version 3.3.12-12704 was used.

Phosphate stabilized Ni in Hi-Sol HDS by forming $Ni_3(PO_4)_2$(s) phase but was under saturated. No phases were formed between $PO_4$ and Pb. Most of the $PO_4$ was precipitated with respect to hydroxyapatite ($Ca_5(PO_4)_3OH$) with a Saturation Index (SI) of 6.8. Other mineral phases that were saturated but not involving $PO_4$ included; Anhydrite ($CaSO_4$), Gypsum ($CaSO_4.2H_2O$) and Alunite ($KAl_3(SO_4)_2(OH)_6$) with SI that ranged from 0.1 to 1.0. Therefore, the added $PO_4$ stabilized mostly Ca. The substantial reduction in the solubility of Ni, Pb and other metals of concern was mainly a contribution of adsorption on the reactive surfaces of saturated phases (Eighmy et al. 1997, Crannell et al. 2000 and Karna et al. 2017) since there were no substitutions identified.

Using a combination of $CaCO_3$ and $Ca(OH)_2$ to treat AMD generated Lo-Sol Mn HDS that showed minimal solubility of metals making it a less risk to the environment. Phosphating this material with $PO_4$, substantially decreased the solubility of metals reducing further its environmental risk. The addition of $PO_4$ at 4000 mg P l$^{-1}$ slightly reduced the pH by 0.4 down to 7.9. There was a complete immobilization of both Ni and Pb. The added $PO_4$ improved the chemical stability of Ni by forming $Ni_3(PO_4)_2$(s) phase although it was undersaturated. Mostly the solution was saturated with respect to $Ca_5(PO_4)_3OH$ that had an SI of 19. Other mineral phases that precipitated but excluded $PO_4$ were $Al(OH)_3$, $CaSO_4$, Boehmite (γ-AlO(OH)), CoSe, Diaspore (α-AlO(OH)), Gibbsite ($Al(OH)_3$)) and $CaSO_4.2H_2O$ with SI ranging from 0.02 to 1.0. There were no phases that were formed between $PO_4$ and Pb. There is possibility that this element, some of the Ni and other metals were adsorbed on the surfaces of saturated phases (Eighmy et al. 1997, Crannell et al. 2000 and Karna et al. 2017)

In summary, the solubility of metals especially Ni in Hi-Sol Mn and Pb in Lo-Sol Mn HDS were chemically stabilized successfully by the addition of $PO_4$ as demonstrated in Table 2. Therefore, both materials can be of low risk to the environment after phosphating. The sequestration of plant nutrients Mn, Fe, P, Ca, Mg and K could be a disadvantage in the short term but can be slowly released through dissolution of e.g. $CaSO_4.2H_2O$ and $Ca(Fe,Mg,Mn)(CO_3)_2$ for the benefit of plants.

### *Does phosphating HDS make it more stable against reduction?*

Manganese electron demand directly determined the oxidation capacity of Mn oxides in HDS, whereas TED estimated the oxidation capacity of both Mn and Fe (Van Bodegom et al. 2002 and Sparks 1993). Amorphous ferrihydrite remained as the predominant Fe source in HDS. As determined by TED, the addition of $PO_4$ from 50 to 6000 mg P l$^{-1}$ significantly decreased reducible Fe in Hi-Sol Mn HDS from 28 to 0.9 mmol e$^-$ (Fig. 1 a). This showed that $PO_4$ prevented the reduction of HDS hence reduced the concentration of $Fe^{2+}$ determined by TED. The added $PO_4$ was adsorbed and formed sparingly soluble complexes with ferrihydrite preventing the reduction of HDS (Cornell and Schwertmann 2003). The addition of $PO_4$ in Lo-Sol Mn HDS from 50 to 6000 mg P $l^{-1}$ facilitated the reduction of this material significantly increasing Fe release from 2.6 to 7 mmol $e^-$. This indicated that phosphating increased TED. A significant increase in the MED from 0.2 to 1.7 mmol $e^-$ in Lo-Sol Mn HDS was achieved by increasing the application rate of $PO_4$ from 50 to 6000 mg P $l^{-1}$ as determined by MED (Fig. 1 a). But in Hi-Sol Mn HDS adding any rate of $PO_4$ could not increase the oxidation capacity of Mn. The reason was that Mn was already oxidised to Mn(III) or Mn(IV). The reason why TED increased is because it seemed that phosphate actually facilitated the oxidation of Mn(II).

### *Reductive promoted dissolution of HDS before and after phosphating*

Generally, the addition of $PO_4$ at 50 and 6000 mg P $l^{-1}$ to both materials significantly reduced the extractability of Fe, Mn and Al (Fig. 1 b) for all extractants. Fe was the most extracted by all extractants in all sludges (before and after phosphating) followed by Al, Mn, Ni and Pb being the least. Ni extracted by all extractants in both HDS before and after treatment was less than 0.014 %, while Pb was 0 %. Mn was extracted mostly from Lo-Sol Mn HDS by dithionite and hydroxylamine. The high concentration of Mn extracted from Lo-Sol Mn HDS was due to the reduction conditions and the existence of PZC of Mn oxides at pH > 7 that prohibited complexation with $PO_4$ (Graham et al. 1988) since the material had a pH of 8.2. Acid ammonium oxalate was not only able to extract most of this Mn oxide from the 6000 mg P $l^{-1}$ phosphated Lo-Sol Mn HDS. The reason was that acid ammonium oxalate enhanced the reduction and dissolution of the highly phosphated HDS releasing both Fe and Mn oxides. Hi-Sol Mn HDS (both phosphated and non-phosphated) had a pH of 5.5, which falls within a pH range 2 – 7 where Mn had a high affinity for $PO_4$ hence the extracted quantities by all extractants were lower (Graham et al. 1988). Fe and Al oxides were significantly extracted mostly from Hi-Sol Mn HDS (both phosphated and non-phosphated) by all extractants.

## Conclusions and recommendations

Phosphating Hi-Sol Mn and Lo-Sol Mn HDS at 4000 mg P $l^{-1}$ substantially reduced the solubility of Mn, Ni, Pb and other metals through adsorption on reactive surfaces of amorphous $Fe(OH)_3$ and precipitation into mineral phases. After $PO_4$ addition, Fe proved to be the most soluble when both HDS were subjected to different reducing extractants, followed by Al, Mn, Ni and Pb being the least. Adding $PO_4$ at 50 and 6000 mg P $l^{-1}$ reduced TED in Hi-Sol Mn HDS, but increased it in Lo-Sol Mn HDS. The addition of $PO_4$ did not change MED for Hi-Sol Mn HDS but increased that of Lo-Sol Mn HDS phosphate at 6000 mg P $l^{-1}$. Phosphating reduced metal solubility and improved both materials towards better plant nutrient sources.

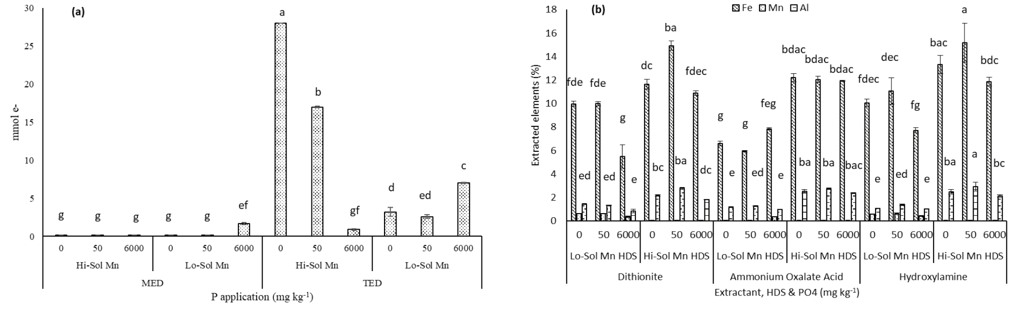

***Fig. 1:*** *a) Mn electron demand and Total electron demand for HDS, b) Fe, Mn and Al extraction by Dithionite, Acid ammonium oxalate and Hydroxylamine in HDS*

## Acknowledgements

The Authors would like to acknowledge the Water Research Commission of South Africa for supporting the study through financial assistance.

## References

Aubé B, Zinck JM (1999) Comparison of AMD treatment processes and their impact on sludge characteristics. Noranda Inco. Technology Centre, 240 Hymus, Blvd Pointe-Claire, Quebec, H9R 1 G5, Canada. Proceedings; 1

Barthel J, Edwards S. (2004) Chemical stabilization of heavy metals. Met. Treat.Technol. MT2 3, 151e162

Bartlett RJ, James BR 1995. System for categorizing soil redox status by chemical field testing. Geoderma, 68: 211-218.

Cornell RM, Schwertmann U (2003) Formation In: The Iron Oxides, Structure, Properties, Reactions,

Occurrences and Uses. Second Completely Revised and Extended Addition. Wiley-VCH Verlag GmbH & Co KGaA, Weinheim. pp 345-407

Courchesne F, Turmel MC (2007) Extractable Al, Fe, Mn, Si, In: Carter RM and Gregory EG (Ed). Soil sampling and methods of analysis, 2nd Ed. Canadian Society of Soil Science. Florida: CRC Press, pp 309-311

Crannell BS, Eighmy TT, Krzanowski JE, Eusden Jr. JD,, Shaw EL, Francis (2000) Heavy metal stabilization in municipal solid waste combustion bottom ash using soluble phosphate Waste Management 20: 135-148.

Eighmy TT, Crannell BS, Butler LG , Cartledge FK, Emery EF, Oblas D, krzanowski JE, Eusden, Jr. JD, Shaw EL, Francis CA (1997) Heavy Metal Stabilization in Municipal Solid Waste Combustion Dry Scrubber Residue Using Soluble Phosphate. Environ. Sci. Technol. 31:3330-3338

Graham RD, Hannam RJ, Uren NC (1988) Inorganic Reactions of Manganese in Soils, In: Manganese in Soils and Plants. Kluwer Academic Publishers, Netherlands. pp 37 - 50

Harris DL, Lottermoser BG (2006) Evaluation of phosphate fertilizers for ameliorating acid mine waste. Applied Geochemistry 21:1216–1225. doi:10.1016/j.apgeochem.2006.03.009

Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Science of the Total Environment 338:3-14

Kalin M, Fyson A, Wheeler WN (2006). The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. Science of the Total Environment 366:395–408

Karna RR, Luxton T, Bronstein KE, Redmon JH, Scheckel KG (2017) State of the science review: Potential for beneficial use of waste by-products for in situ remediation of metal-contaminated soil and sediment, Critical Reviews in Environmental Science and Technology, 47:2, 65-129, DOI: 10.1080/10643389.2016.1275417

Kumpiene J, Lagerkvist A, Maurice C (2007) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Management 28:215–225

Loubser G, Verryn S (2008) Combining XRF and XRD analyses and sample preparation to solve mineralogical problems. South African Journal of Geology.111:229-238

Lottermoser BG (2007) Mine water, In: Mine Wastes, Characterization, treatment, environmental impacts, 2nd Ed. Springer-Verlag Berlin Heidelberg, pp 139-140

Loubser G, Verryn S (2008) Combining XRF and XRD analyses and sample preparation to solve mineralogical problems. South African Journal of Geology.111:229-238

Maree JP, Strydom WF, Adlem CJL, De Beer M, Van Tonder GJ, Van Dijk BJ (2004) Neutralization of Acid Mine Water and Sludge Disposal. Division of Water, Environment and Forestry Technology CSIR. WRC Report No 1057/1/04

Method 3051A, Revision V (2014) Final Update II to the Third Edition of the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846.

Thomas GW (1996) Soil pH and Soil Acidity. In: Methods of Soil Analysis, Part 3 – Chemical methods. SSSA Book Series No. 5, pp 475

United States Environmental Protection Agency (EPA) (1992) SW-846 Test Method 1311: Toxicity Characteristic Leaching Procedure (TCLP). https://www.epa.gov/hw-sw846/sw-846-test-method-1311-toxicity-characteristic-leaching-procedure. Accessed 9 March 2017

Van Bodegom PM, Van Reeven J, Van Der Gon HACD (2003) Prediction of reducible soil iron content from iron extraction data. Biogeochemistry 64:231-245.

Wilmoth RC (1977) Limestone and lime neutralization of ferrous iron acid mine drainage. Environmental Protection Technology Series. EPA-600/2-77-101

Zinck JM (2006) Disposal, reprocessing and reuse options for acidic drainage treatment sludge. American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

Zinck JM, Wilson LJ, Chen TT, Griffith W, Mikhail S, Turcotte AM (1997) Characterization and Stability of Acid Mine Drainage Treatment Sludges. Mining and Mineral Sciences Laboratories Report MMSL 96-079 (CR). MEND Project 3.42.2a, Job No. 51144, Canada. http://mend-nedem.org/wp-content/uploads/2013/01/3.42.2a.pdf. Accessed 28 April 2016