

Pilot Scale Application of Attapulgitic Clay for Stabilization of Toxic Elements in Contaminated Soil

V. Zotiadis¹; A. Argyraki²; and E. Theologou³

Abstract: This study presents an in situ pilot-scale application of attapulgitic clay for stabilization of toxic metals and metalloids in contaminated soil. The selected field for the pilot-scale experiment was heavily contaminated with toxic metals and metalloids in total (Cu: 122 mg/Kg, Pb: 6,610 mg/Kg, Zn: 3,630 mg/Kg, Cd: 26.3 mg/Kg, Ag: 9.4 mg/Kg, As: 802 mg/Kg, Mn: 1,435 mg/Kg, Ba: 304 mg/Kg, Sb: 95.3 mg/Kg) and leachable concentrations. Geochemical and physical properties of treated soil were thoroughly studied before and after mixing with the attapulgitic clay. Soil mineralogy was determined by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. On the basis of the site specific soil geochemical properties, appropriate proportion of specific grain size attapulgitic clay was added and mixed in situ with simultaneous adjustment of soil moisture content to reach saturation. Analytical data of amended soil samples collected 1 month after the application showed a significant reduction of water leachable metal fraction (Cu: 17%, Pb: 50%, Zn: 45%, Cd: 41%, Ag: 46%, As: 18%, Mn: 47%, Ba: 45%, Sb: 29%). In addition, soil pH was stabilized at slightly alkaline conditions and remained constant during a 7-month monitoring period after amending the soil. Overall, the use of attapulgitic clay as a binder for immobilizing metals in contaminated land is a promising stabilization method at a competitive cost under present market conditions. DOI: [10.1061/\(ASCE\)GT.1943-5606.0000620](https://doi.org/10.1061/(ASCE)GT.1943-5606.0000620). © 2012 American Society of Civil Engineers.

CE Database subject headings: Remediation; Clays; Soil stabilization; Soil pollution; Heavy metals.

Author keywords: Remediation; Attapulgitic clay; In situ; Stabilization; Pilot-scale toxic elements.

Introduction

Stabilization methods utilizing mineral-based materials are routinely used in the remediation of contaminated land (O'Day and Vlassopoulos 2010). Laboratory scale environmental applications of attapulgite in remediation of contaminated land and groundwater have previously been described by many researchers (Zhen Li et al. 2006; Álvarez-Ayuso et al. 2003; Diaz et al. 2007; Veli et al. 2007; Potgieter et al. 2006; Shirvani et al. 2006). However, there are not any studies on larger scale experiments involving applications in the field. This study presents an in - situ pilot-scale application of attapulgitic clay for stabilization of toxic metals in contaminated soil.

Materials and Methods

Attapulgitic Clay

Attapulgite, (palygorskite) structure consists of modulated 2:1 layers, demonstrating a variable dioctahedral to trioctahedral

character expressed by the following general chemical formula: $Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ (Galan 1996; Gionis et al. 2006). The attapulgitic clay used in this study originated from the Pefkaki deposit at Grevena, Greece (Kastritis et al. 2003). Its specific surface area (SE) was measured equal to 120 m²/g by single point BET N₂ adsorption method, and the pH was measured potentiometrically equal to 9.1 after mixing with distilled water in a 1:5 ratio. Cation exchange capacity (CEC) was measured equal to 25 meq/100 g determined by the ammonium acetate method. Table 1 presents chemical analysis data of two representative attapulgitic clay samples analyzed for major elements (oxides %) by inductively coupled plasma-mass spectrometry (ICP-MS) after total dissolution.

Semiquantative mineralogical analysis using X-ray diffraction (XRD) and chemical analysis of the used attapulgitic clay identified the following mineral phases: attapulgite (65%), saponite (25%), quartz (6%), and serpentine (4%). Physical properties were determined by geotechnical laboratory tests (Table 2). The sample was characterized as a micronized, lightweight material (dry bulk density < 7 KN/m³ by ASTM D6683-01) and was classified as elastic silt (MH).

Study Area

The selected field for the pilot-scale experiment is located in Lavrion town, 55 km southeast of Athens, Greece. More than 3,000 years of intensive mining and metallurgical activities of exploiting the silver-bearing galena ore have created a vast amount of exposed toxic waste (Marinos and Petrascheck 1956; Demetriades 2010). The particular field that was used in this study lies within a public recreational area. Field dimensions were 9 × 12 m, and the overburden material consisted of a mixture of alluvial soil and mining/metallurgical waste at least to a depth of 30 cm.

¹Environmental Consultant, Edafomichaniki S.A., Em. Papadaki 19, 14121 Athens, Greece.

²Assistant Professor, Dept. of Economic Geology and Geochemistry, National and Kapodistrian Univ. of Athens, Panepistimiopolis Zographou, 15784 Athens, Greece (corresponding author). E-mail: argyraki@geol.uoa.gr

³Environmental Geologist, Dept. of Economic Geology and Geochemistry, National and Kapodistrian Univ. of Athens, Panepistimiopolis Zographou, 15784 Athens, Greece.

Note. This manuscript was submitted on January 28, 2011; approved on August 16, 2011; published online on August 18, 2011. Discussion period open until October 1, 2012; separate discussions must be submitted for individual papers. This technical note is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 138, No. 5, May 1, 2012. ©ASCE, ISSN 1090-0241/2012/5-0-0/\$25.00.

Table 1. Chemical Composition of the Used Attapulgitic Clay Sample

Major elements oxides (%)	Attapulgitic clay (Sample 1)	Attapulgitic clay (Sample 2)
SiO ₂	62.2	62.4
Al ₂ O ₃	5.63	5.93
Fe ₂ O ₃	8.57	9.12
MgO	9.67	10.11
CaO	0.67	0.74
Na ₂ O	0.162	0.168
K ₂ O	0.373	0.361
TiO ₂	0.258	0.284
MnO	0.015	0.016
P ₂ O ₅	0.014	0.014
LOI	12.2	11.4
Total	99.8	100.5

Note: LOI = loss of ignition.

Preparation of the Field and Soil Treatment Activities

Preparation of the study area included rotor-tilling to a depth of 30 cm, manual removal of large cobbles and rewetting the soil to amend the initial soil moisture content. Three-fold composite samples (10–20 cm depth) were thereafter collected on a regular grid. A preliminary lab-scale study was performed by using a composite soil sample from the studied field for determining the appropriate soil/attapulgitic clay mixing proportion and to provide reference for comparison with findings from the pilot-scale field application.

The results, presented in Fig. 1, indicated that increasing the mixing quantity of attapulgitic clay reduces the water leachable fraction of studied metals in soil until a critical proportion of 4% is reached. Beyond this optimum mixing proportion, metal concentrations reach a plateau, and no further change is observed. Thus, subsequent soil treatment included addition of appropriate amount of attapulgitic clay, mixing, homogenization, and rewetting to attain near saturated conditions. Homogenization of treated soil was repeated on a weekly basis for a 1 month period (4 weeks), using a rotor-tiller in parallel with soil rewetting to maintain near-saturation soil conditions. Soil pH was monitored weekly. A final set of samples was collected at the end of the 4-week period to study the final geochemical characteristics of the study area,

Table 2. Physical Properties of Attapulgitic Clay and Untreated Soil

Gravel ^a		Sand ^a			Silt ^b	Clay ^b	LL ^c (%)	PL ^c (%)	Moisture content ^d (%)	USCS
Coarse	Fine	Coarse	Medium	Fine						
Attapulgite										
				3.5	23.1	73.4	169	76	< 0.5	MH
				3.0	24.6	72.2	163	75	< 0.5	MH
Untreated soil										
14.9	21.7	12.1	17.6	17.5	13.8	2.4	NP	NP	1.7	SM
17.3	15.1	8.5	15	18.1	21.4	4.7	30	NP	2.1	SM
28.8	14.4	7.9	13.1	14.8	18.9	2.5	31	NP	1.2	GM
23.5	15.7	8.3	13	16.2	19.1	4.2	28	NP	2.0	GM
15.7	18.9	8.5	13.9	19.5	18.2	5.3	28	NP	1.7	SM

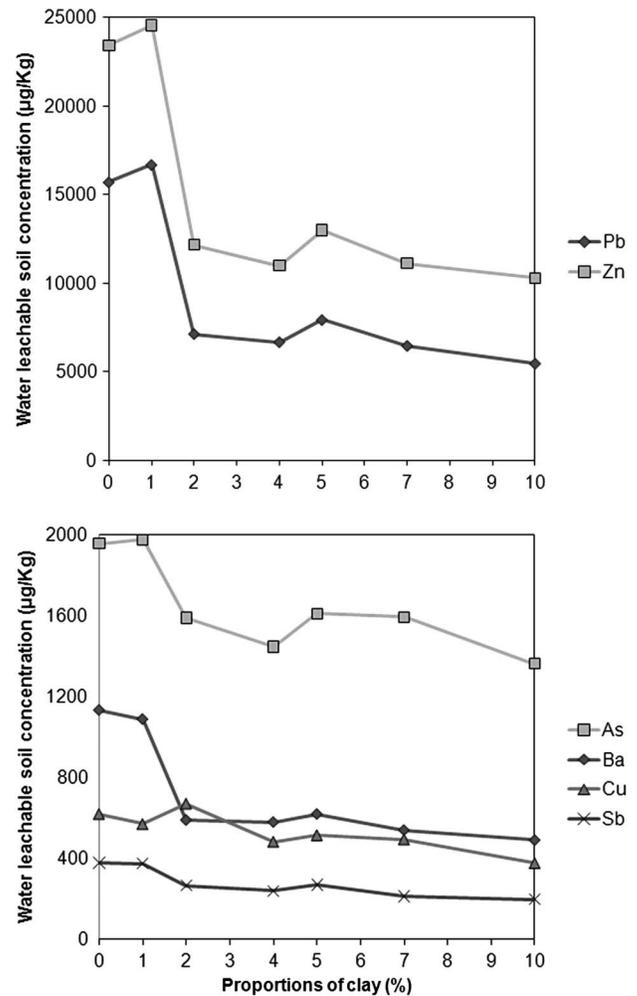
Note: NP = nonplastic, LL= liquid limit, PL= plasticity limit, USCS = unified soil classification system.

^aASTM C136-06.

^bASTM D422-02.

^cASTM D4318-05.

^dASTM D2216-90.

**Fig. 1.** Water leachable soil concentrations of: (a) Pb, Zn; (b) As, Ba, Cu, Sb after treatment with various proportions of attapulgitic clay in the laboratory scale experiment

whereas pH monitoring continued for a period of 7 months on a monthly basis.

Sampling, Chemical, and Mineralogical Analysis

A total of 24 composite soil samples were collected from the field for chemical analysis, 12 before and 12 after treatment with attapulgite clay. Chemical analysis was performed on dried samples of $-100\ \mu\text{m}$ to determine the concentration of 10 metals using ICP-MS after total digestion. Analytical bias was estimated by analyzing the NIST certified reference material SRM2711 within the same analytical batch. Analytical precision was assessed by using analytical duplicates.

Leaching experiments were conducted on 12 subsamples of untreated soil samples and 12 subsamples of attapulgite treated soil. A mixing ratio of 1:20 soil to deionized water was used for the leaching experiments. Samples were agitated for 2 hours at room temperature and were analyzed to determine elemental concentrations by ICP-MS. The analytical precision of these measurements was better than $\pm 5\%$ assessed by analytical duplicates, allowing further interpretation of the geochemical data. Soil pH was determined potentiometrically in composite soil samples after mixing with distilled water at a ratio of 1:2.

Results and Discussion

Physical properties of untreated contaminated soil were determined by geotechnical laboratory tests (Table 2). Mineral phases in untreated soil samples including quartz, calcite, albite, illite, and chlorite were identified by XRD analysis. Slag material, iron and zinc oxides, and minor phases of secondary minerals, such as hydrocerussite, were determined by scanning electron microscope energy dispersive spectroscopy (SEM-EDS) analysis (Fig. 2). Microanalysis of slag grains indicated Al, Ca, Fe silicate phases, Pb-As oxides, and Fe oxides to be the most important heavy metal bearing phases in soil.

The measured total concentrations of Pb, Zn, As, Cd, and Sb in soil greatly exceeded the corresponding intervention values established by the “New Dutch List” ([Ministry of Housing, Spatial

Table 3. Total Elemental Concentrations in Untreated Soil Samples ($n = 12$)

Element	Mean	Minimum	Maximum	Standard deviation	Intervention values ^a
Cu	122	88	136	17	190
Pb	6,610	4,516	7,869	1,074	530
Zn	3,630	2,706	4,281	595	720
Ag	9.4	1.4	7.0	10.8	15
Mn	1,435	164	1,130	1,616	—
As	802	511	1,003	166	76
Cd	24.5	19.5	28.9	3.6	13
Sb	95	66	106	15	22
Ba	304	247	682	135	920

Note: Values in mg/kg.

^aVROM (2009).

Planning and Environment (VROM 2009)], indicating high poly-metallic soil pollution (Table 3).

The descriptive statistics of water leachable concentrations in untreated and treated soil samples are presented in Table 4. Before treatment the determined water leachable metal exceeded the limit values for inert waste assigned by Directive 2003/33/EC (European Union 2002). Consequently, the measured water leachable metal concentrations pose significant environmental risk confirming the need for reducing potentially toxic elements’ mobility by using a stabilization method. Water leachable concentrations after treatment indicate that the performed remediation method reduced significantly the readily bioaccessible water leachable fraction of metals and subsequently, the associated exposure risk to humans and biota.

The increase of soil pH is an important mechanism in metal stabilization techniques (USEPA 2003). In this study, the addition of attapulgite clay to soil gradually modified and maintained soil pH levels between 8.0 and 8.2 (Fig. 3).

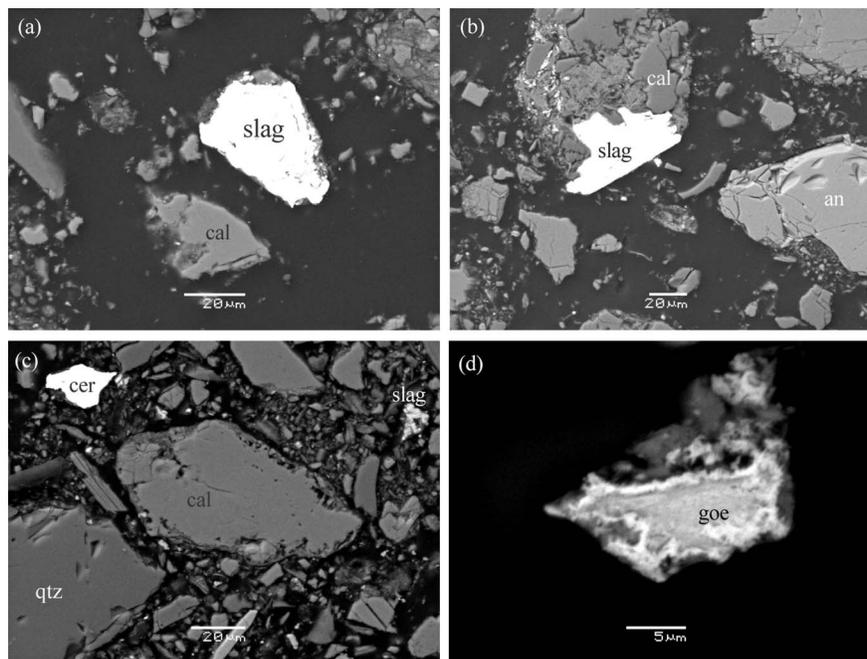
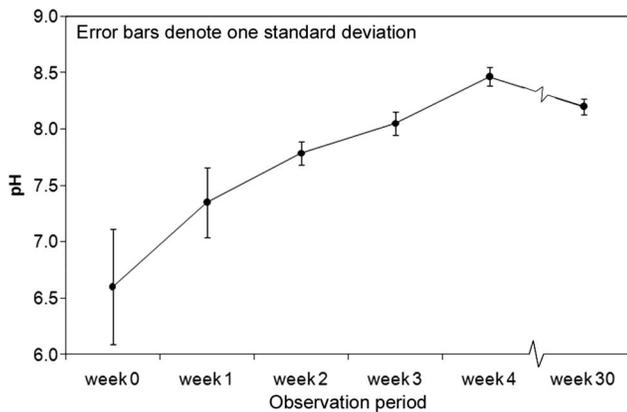


Fig. 2. Microphotographs of SEM backscattered emission showing nonmetallic and metallic soil grains in untreated samples: (a) calcite (cal) and heavy metal bearing slag grains; (b) calcite (cal) in close association with slag material rich in Pb and As and anorthite (an) grain; (c) grains of calcite (cal), cerussite (cer), quartz (qtz), and eroded Al, Ca, and Fe silicate slag grain; (d) goethite grain (goe) enriched in heavy metals

Table 4. Water Leachable Elemental Concentrations before and after Treatment of Soil Samples with Attapulgitic Clay ($n = 12$)

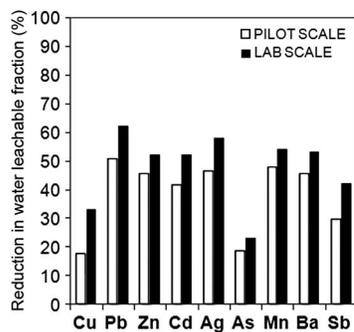
Element	Mean		Minimum		Maximum		Standard deviation	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Cu	544	456	505	329	577	537	34	83
Pb	9,198	4,609	6,491	3,146	11,109	6,267	2,325	1,179
Zn	12,848	7,006	9,170	4,770	15,710	9,210	3,253	1,803
Ag	18	9	14	6	20	12	3	2
Mn	2,666	1,416	1,780	780	3,330	2,220	800	471
As	1,455	1,190	1,312	857	1,554	1,487	128	224
Cd	40	24	31	20	51	27	8	3
Sb	232	165	203	138	256	169	26	12
Ba	580	312	420	150	710	530	131	186

Note: Values in $\mu\text{g}/\text{kg}$.

**Fig. 3.** Change of pH in attapulgite treated soil samples over a 30-week observation period

To better assess the effectiveness of the performed pilot-scale stabilization technique, the pilot-scale field results were compared with the corresponding data from the lab-scale study (Fig. 4), and results did not present substantial differences from those anticipated during initial planning of the experiment.

The effectiveness of metal stabilization techniques on soil depends on numerous factors beside the type of binder, including physical (e.g., grain size, plasticity, permeability, and moisture content) and geochemical characteristics (e.g., type of contaminant, concentration, heterogeneity, leachability, mineralogy, pH, and Eh) of the soil and on other competitive factors (USEPA 2003).

**Fig. 4.** Comparison of reduction (%) in water leachable metal fraction between pilot field scale and laboratory scale application

Soil solution pH is an important variable that controls the adsorption of the metal at clay water interfaces. Clays are known to possess a negative surface charge in solution. Potgieter (2006) showed that at slightly alkaline conditions more, of the positively charged metal ions are adsorbed on the negative clay surface, and precipitation of metal hydroxides occurs. Alvarez-Ayuso et al. (2003) suggested that reaction of heavy metals with numerous silanol groups is the major mechanism responsible for metal ions sorption on palygorskite. Shirvani et al. (2006) also suggested two possible mechanisms for adsorption, i.e., replacement of Mg^{2+} in the edges of octahedral layer and inner-sphere complexation on the functional groups on the broken edges of the mineral and subsequent release of H^+ . Furthermore, data of Cai and Xue (2008) from desorption experiments on four Cu-adsorbed palygorskites combined with spectroscopic observations confirmed three possible mechanisms for copper adsorption by palygorskite: (a) Cu is adsorbed onto the surface or in a netlike interstice; (b) Cu forms a complex ion $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and is trapped in the channel; or (c) Cu enters into the hexagonal channel of the tetrahedral sites or the unoccupied octahedral sites of palygorskite.

In general, the effectiveness of the attapulgitic clay as a binder for toxic elements stabilization in contaminated soil is attributed to a combination of factors such as (a) direct control and time sustention of soil pH levels to slightly alkaline, (b) high adsorption capacity as a result of the high specific surface area, and (c) sorption capacity derived by the existence of nanopores within the free channels of mineral structure. Further experiments are required to clarify which is the dominant process controlling the observed reduction of water leachable metal concentrations after treating this particular soil with attapulgitic clay.

Conclusions

This study demonstrated the feasibility of applying attapulgitic clay as a binder insitu for stabilization of toxic metals in contaminated soil at a pilotscale. The optimum mixing ratio of attapulgitic clay to contaminated soil for this particular site was determined at 4% by a preliminary lab-scale study. The corresponding reduction of water leachable metal fraction of metals in pilot-scale application was determined as high as 17% for Cu, 50% for Pb, 45% for Zn, 41% for Cd, 46% for Ag, 18% for As, 47% for Mn, 45% for Ba, and 29% for Sb. Overall, the pilot-scale stabilization method using attapulgitic clay as an additive for immobilizing metals in contaminated soil is a promising and cost-effective remediation technique under present market conditions.

References

- Álvarez-Ayuso, E., and García-Sánchez, A. (2003). "Palygorskite as a feasible amendment to stabilize heavy metal polluted soils." *Environ. Pollut.*, 125(3), 337–344.
- Cai, Y. F., and Xue, J. Y. (2008). "A study of adsorption and absorption mechanisms of copper in palygorskite." *Clay Miner.*, 43(2), 195–203.
- Demetriades, A. (2010). "Medical geology in Hellas: The Lavrion environmental pollution study." *Medical geology: A regional synthesis*, O. Selinus, et al., eds., Springer, Dordrecht, Netherlands, 355–390.
- Diaz, M., Cambier, P., Brendlé, J., and Prost, R. (2007). "Functionalized clay heterostructures for reducing cadmium and lead uptake by plants in contaminated soils." *Appl. Clay Sci.*, 37(1–2), 12–22.
- European Union. (2002). *Establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC*, Council Directive 2003/33/EC, Official Journal of the European Union, L11/27–49.
- Galan, E. (1996). "Properties and applications of palygorskite-sepiolite clays." *Clay Miner.*, 31(4), 443–453.
- Gionis, V., Kacandes, G. H., Kastritis, I. D., and Chryssikos, G. D. (2006). "On the structure of palygorskite by mid- and near-infrared spectroscopy." *Am. Mineral.*, 91(7), 1125–1133.
- Kastritis, I. D., Mposkos, E., and Kacandes, G. H. (2003). "The palygorskite and Mg-Fe smectite clay deposits of the Ventzia basin, Western Macedonia, Greece." *Mineral Exploration and Sustainable Development, Proc., 7th SGA Meeting*, D. Eliopoulos, et al. eds., Millpress, Rotterdam, Netherlands 891–894.
- Marinos, G. P., and Petrascheck, W. E. (1956). "Lavrion." *Geological and geophysical research 4:1*, Institute for Geology and Subsurface Research, Athens (in Greek with English summary).
- Ministry of Housing, Spatial Planning and Environment (VROM). (2009). "Soil remediation circular 2009." Directorate General For Environmental Protection, Netherlands.
- O'Day, P. A., and Vlassopoulos, D. (2010). "Mineral-based amendments for remediation." *Elem.*, 6(6), 375–381.
- Potgieter, J. H., Potgieter-Vermaak, S. S., and Kalibantonga, P. D. (2006). "Heavy metals removal from solution by palygorskite clay." *Miner. Eng.*, 19(5), 463–470.
- Shirvani, M., Kalbasi, M., Shariatmadari, H., Nourbakhsh, F., and Najafi, B. (2006a). "Sorption-desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: Isotherm hysteresis." *Chemosphere*, 65(11), 2178–2184.
- Shirvani, M., Shariatmadari, H., Kalbasi, M., Nourbakhsh, F., and Najafi, B. (2006b). "Sorption of cadmium on palygorskite, sepiolite and calcite: Equilibria and organic ligand affected kinetics." *Colloids Surf. A*, 287(1–3), 182–190.
- U.S. EPA. (2003). "Guidance on the use of stabilisation/solidification for the treatment of contaminated soil." *R&D Technical Rep. P5-064/TR/1*, Washington, DC.
- Veli, S., and Alyüz, B. (2007). "Adsorption of copper and zinc from aqueous solutions by using natural clay." *J. Hazard. Mater.*, 149(1), 226–233.
- Zhen, L., Lin, Y., and Kun, H. (2006). "Iron-rich palygorskite: A potential clay material for contaminated environment remediation." *Chin. J. Geochem.*, 25(Suppl. 1), 109–110.