The morphology and elemental variation for contaminated clay soil using Energy Dispersive X-Ray Spectrometry

K A Saeed¹ and S A Hashim²
¹ Lecturer, Water Resources Department, Mustansiriyah University, Baghdad, Iraq,
² Asst. Prof., Water Resources Department, Mustansiriyah University, Baghdad, Iraq,

Email: khitamhussein@yahoo.com

Abstract It is known that the stabilization of normal soils with chemical substances will gradually affect their properties like shape, size and soil particles arrangement. The current study concerns with artificially contaminated clayey soils immobilized by fly ash waste materials and quicklime (CaO). In this research, the time-dependent factor changes the morphology of stabilized – contaminated soil. Energy Dispersive X-ray Spectrometry is performed to further examine components on the clay particles’ surface. The results showed that with an increase in hardening time, morphology analyses by FESEM shows a transformation of soil fabric due to the effect of chemical treatment, and due to the production of cementitious pozzolanic compounds (CSH and CASH). However, with the presence of contamination, it can notice a transformation in the fabric of clay particles towards a more flaky nature at the early curing time due to precipitation of heavy metals as hydroxide or sulphates on the surface of particles. Regarding the EDAX analysis, the Al:Si ratio for cement-fly ash treated clayey soil decreases over time. This is attributed to the increased release of alumina from the mineral of clay structure. However, an increasing Ca:Si ratio is observed, especially after 100 days related to the formation of the portlandite compound from cement hydration over time. While, it is detected variation in these ratios with respect to contaminated soil with time.

1. Introduction

Heavy metal contamination is a common problem that is encountered at many uncontrolled sites. Thus, there is increasing interest in treatment of contaminated soil to enable environmentally responsible reuse applications and circumvent the need for costly landfill disposal. Concerning the harmful effects of the environment contamination has increased meaningfully over the past two decades through the active participation of environmental groups. Thus, the disposal of chemical contamination has become one of the major problems currently faced by the environment. These contaminants include sedimentation in rivers, canals, lakes and reservoirs as a result of air and/or water transport as well as direct contact with land [1]. Therefore, any readily applicable technology that easily handles large amounts of contaminated soil and sedimentation that does not require excessive amounts of expensive additives, is of great importance.

Thus far, numerous mechanisms have been established to treat polluted sites, which alter hazardous non-toxic waste or reduce the latent release of toxic species into the environment. Stabilization/solidification (S/S) is one of these methods to stabilize the solid wastes and contaminants by addition of traditional cementitious additives, such as hydrated lime, cement, and fly ash [2 and 3]. Fly ash can be admixed to this wastes (contaminated soil) to rise the obtainable pozzolanic surface area and therefore, to develop the properties of this waste mixture like the strength and heavy metal
leachability. Fly ash class C was applied effectively in many constructions because of its high calcium content and its self-cementing properties [4]. While, the other type of fly ash is a low calcium content (fly ash class F), which is created by the combustions of lignite coal. The fly ash class C when mixed with lime will initiate pozzolanic reactions, leading to production of cementitious product like Calcium Aluminium and Calcium Silicate Hydrate, CAH and CSH as stated by [5].

Furthermore, fly ash is considered as a waste in itself. The addition of fly ash to stabilize a polluted environment would be a great way to eliminate pollution. Appropriate technical control would lead to be cost-effective technique by decreasing disposal expenses and reducing potential negative results.

When adding large quantities of lime to the fly ash combination, the pH of the unstable lime blend is increased to about 12.8, the pH of the ‘saturated’ lime water. It is actually a high pH as compared to the pH of normal soil sediments, which is generally between 5 and 8. Therefore, in this case, the solubility of silica, alumina in the mixture of fly ash, and clay minerals developed significantly at these high pHs. They are therefore, accessible to react with calcium from lime and/or fly ash to produce cement hydrates (CAH and CSH). It should be noted, that the creation of these cementitious compounds are mainly responsible on the improved the properties of the stabilized contaminated soils.

In this study, the changes induced in clay-sand soil-stabilizer-metals matrix along curing time, were detected by Energy Dispersive X-ray Spectrometry (EDAX) and Field Emission Scanning Electron Microscopy (FESEM). Thus, to achieve the objectives of the study, a laboratory estimation of contaminated soil combinations treated with quicklime and fly ash was carried out.

2. Materials and Experimental Programmes

2.1. Soil and Stabilizers
In this study, silty clay soil samples were selected, which consist of clay minerals (kaolinite mixed with fine quartz). As observed from the image of energy dispersive X-ray spectrometer (EDAX) in Figure 1, there were elevated heights of iron (Fe) peaks that refer to the existence of iron oxides on the surface of the clay particles as stated by [6]. Selected heavy metals were mixed with the natural soil to produce artificially contaminated soil. The ‘physical properties’ and ‘chemical composition’ of the investigated soil is presented in table 1.

Figure 1. EDAX Spectrum of natural soil
It should be noted, that the use of a traditional stabilizer such as lime alone may lead to unsatisfying results and may not encounter the necessities for reuse in the construction requests. This was due to lack of aluminates and silicates in the granular material, and then, pozzolanic reactions may not occur in these soils. In addition, the presence of containates can lead to inhibiting the geotechnical properties of soils. For this reason, another additive stabilizer was used in this study named Fly ash class C to growth the existing Pozzolanic of surface area, and then progress physicochemical properties of contaminated soils. As reported by [7, 8, and 9], fly ash has artificial pozzolans that react with lime to increase the strength of soil progress through cementing its particles. To ensure the proportionate of chemical composition, the lime utilized in this study has been kept at a elevated temperature oven to prevent the progressive accumulation of particles. This study was conducted on artificially contaminated soils, equipped in the laboratory and containing’ lead (Pb+2), chromium (Cr^3+ and Cr^6+) and Cu^{2+}.

2.2. Preparation of Specimens

The heavy metal contents that are selected in this study to produce the artificial soils were (5000 mg/kg, 650 mg/kg, and 720 mg/kg) of each of Cr(NO_3)_3, PbO, and Cu(NO_3)_2, respectively. It should be noted, due to the limitation of the selected suitable contents of the stabilizers to develop contaminated soil, it had been depended on the previous studies conducted regarding to the stabilizer content which are essential for modification and pozzolanic reaction as reported by [10, 11, 12, and 13]. Therefore, depending on the appropriate proportions of binders for pozzalanic reaction and to reducing the cost, it was selected 5% as the appropriate content for lime as a fixed content.

In this study, 5, 10, and 15 were used as percentages for fly ash whereas the lime was used in percentage of 5 only [14]. The required quantities of samples were provided by cracked, air-dried,

| Table 1. The physical properties and chemical composition for selected soil |
|---------------------------------------------------------------|
| **Engineering and physical properties** | **Chemical compositions oxides** | **values** |
| CEC(meq/100) | SiO_2 | 12.87 |
| pH(L/S= 2.5) | Al_2O_3 | 4.34 |
| Specific gravity | Fe_2O_3 | 1.03 |
| Liquid | K_2O | 4.01 |
| Limit, LL(%) | SO_3 | 2.07 |
| Plastic Limit, PL(%) | CO_2 | 1.34 |
| Plasticity Index, PI(%) | soluble(Al) | 5.8ppm |
| Max. Dry. Density (Mg/m3) | soluble(Si) | 4ppm |
| Optimum Moisture Content (%) | soluble(Ca) | 0.4ppm |
| | 24.3 |

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smaller-sized soil and screened with a 2-mm sieve. The sieving was prepared confirming that the soil was of uniformed status.

Time-dependent factor effect of soil stabilized with lime-fly ash was examined. When heavy metals were added to the mixtures, the optimum water contents of the respective un-contaminated sample were used, thus allowing for direct comparison of the effects of contaminant. The BS 1377: Part 4: 1990 is (clause 3.3.4.1)[15] was applied to define the compaction properties, which was accomplished by packing the soil using Proctor mould. After compacting the soil into a standard mold which has the dimensions of (76 mm length and diameter 38 mm) with a constant compaction force according to BS1924: Part 2 1990 (Section 4.1.5) [15], the specimen was extracted with a hydraulic jack. Then they were enveloped in a tight plastic film and put in a plastic receptacle with an inflexible cap to inhibit moisture loss during the drying time. After that, samples have been kept at room with organized temperature (27±2°C) till the required period to inspect them at each of the five times of curing, which were (7 days, 14 days, 28 days, 100 days, and 200 days). It should be mentioned that curing condition is effective in the case of contaminated samples to estimate the effects of these contaminants on the soil characteristics for the short and long term.

2.3. Testing program
In this study, A JSM-6701F JEOL Field Emission Scanning Electron Microscope (FESEM) has been applied to investigate the morphological modifications and topographic structures related with clay particles due to the treatment process, and due to contamination. Various ‘FESEM’ images were acquired for mixtures with magnifications of 1000× 5000× and 10000. Furthermore, it was supplied with a ‘energy dispersion x-ray spectrometer (EDAX)’, that allowed more differentiated approach to the structure of the system of particle surface at diverse periods of time. The EDAX was applied by performing analyses of selected point locations on the sample. However, it has been well known that the remediation of natural soil contaminated with chemical additions progressively influences the size, shape and organization of the particles of soil. Finally, unconfined compressive strength test was applied to assess the amount of enhancement in the properties of stabilized soil as a result of the establishment and strengthen of cementitious materials.

3. Results and Discussion
Figure 2 shows the micrograph of natural clay soil. It can be seen a free oxides within its microstructure coated and bonded with clay particles. microstructure with platy clay particles in a scattered composition.

![Figure 2. FESEM image of natural untreated soil](image-url)
However, to detect the effects of additives of ‘lime and fly ash’ on the microstructure and morphology of these samples, Scanning Electron Microscope (SEM) was used to visually examine hydration products and micro-structural changes in the matrix of lime-fly ash-heavy metals matrix. Figure 3a shows the micrographs of sample (L0C15: 0% lime+15%fly ash) at 7 days. While figures 3b, c, d show the morphology textures for fly ash stabilized contaminated soils with presence of lime at 7,100, and 200 days curing time. As comparison with figure 3a (no lime), L0C15 samples at 7day show little changes in the texture of the soil matrix. Little flocculation was detected with small signs of Ca(OH)₂ as dedicated by X-ray diffraction. However, by 100 and 200 days, crystalline formations and the ‘fabric’s texture’ of the lime-fly ash treated soil matrix had improved, recognized by the formation of ‘white lumps’. These modifications were assigned to the progression of lime’s production of calcium alumina silicate hydrates.

Energy Dispersive X-ray Spectrometry (EDAX) has been undertaken in this study to further examine elements on the surface of clay particles as well. To observe relative elemental variations due to effects from stabilizers and contaminants, peak intensity at different intervals was recorded.

![Figure 3. FESEM Micrographs of a (L0C15-7days), b (L5C15- 7days), c (L5C15-100days)](image)

Figures 4a, 5a, and 6a present EDAX spectra for samples (L5C15: 5% lime + 15% fly ash) at 7, 100, and 200 curing days, respectively. Furthermore, to evaluate the effects of heavy metals on elemental changes in treated samples over long term curing, figures also show spectra for lime-fly ash treated soils contaminated by heavy metals as presented in figures 4b, 5b, and 6b. High intensity peaks for silicon (Si), aluminum (Al), and iron (Fe) were noted in all samples but in different degrees for each. These elements, particularly iron, improved the lateritic nature of the soil along with the existence of free oxides on clay particle surfaces as stated by [6]. Moreover, calcium (Ca) was observed in treated samples, due to the presence of portlandite within fly ash.

Reliant on variations in Al : Si and Ca : Si ratios in clay soil mixes are presented in table 2. There were imperceptible changes in Al:Si ratios for all samples of lime-fly ash-treated and treated-contaminated soils over different curing intervals. Samples treated ratios varied <10% compared to untreated soil ratios. Lime-fly ash-treated soil Ca:Si ratios increased significantly over time and may
be related to the growth of a micro-structure gel compound with stabilizing ions on clay particles surface [16]. The increasing Ca:Si ratio for contaminated samples were noticeable as compared to uncontaminated samples. This may be due to the lack of cementitious compounds containing silica as a result of retardation by heavy metals.

**Figure 4.** (a) EDAX spectrums of lime-fly ash treated soil without contamination of heavy metals, and (b) with contamination of heavy metals at 7 days curing time.

**Figure 5.** (a) EDAX spectrums of lime-fly ash treated soil without contamination of heavy metals ,
and (b) with contamination of heavy metals at 100 days curing time.

![EDAX spectrums of lime-fly ash treated soil without contamination of heavy metals, and (b) with contamination of heavy metals at 200 days curing time.](image)

**Figure 6.** (a) EDAX spectrums of lime-fly ash treated soil without contamination of heavy metals, and (b) with contamination of heavy metals at 200 days curing time.

| Sample description | Ratio (weight %) |
|--------------------|------------------|
|                    | Al:Si            | Ca:Si         |
| **Mix design**     | **Curing time (days)** |    |    |
| L5C5               | 7                | 1.1          | 0.2 |
| L5C5               | 7                | 1.035        | 0.628 |
| (5%lime+5%flyash)  |                  |              |     |
| L5C10              | 100              | 1.14         | 0.33 |
| L5C10              | 100              | 1.08         | 0.36 |
| (5%lime+10%flyash) |                  |              |     |
| L5C15              | 200              | 1.08         | 0.45 |
| L5C15              | 200              | 1.01         | 0.46 |
| (5%lime+15%flyash) |                  |              |     |

**Table 2.** Variation of Al:Si and Ca:Si ratios for various cement laterite clay soil samples with different curing time

Related to strength development, Figures 7 and 8 show the compressive strength is increased for lime-fly ash stabilized contaminated soil. It can be observed that the compressive strength of soils
contaminated with 5% lime and different percentages of fly ash (5% C, 10% C and 15% C) is increasing more than samples with 0% lime. It can be seen that this increase in strength increases with increasing content of fly ash and over time. Therefore, the time factor can be considered as an effective parameter to improve the resistance in contaminated soils [17]. As shown in Figure 8, however, when treated with 5% lime and as compared with the lime of Fig. 8, this may indicate the increase in resistance values after addition of lime to 200 days. This indication is linked to the fact that class C fly ash in the existence of lime is a preferable means of increasing strength, mainly for weak soils [3]. Overall, the treatment of lime-fly ashes has led to an increase in strength values of over 1000 times compared to values for untreated soil.

![Figure 7](image1.png)  
**Figure 7.** The variations of unconfined compressive strength with different curing times for (0%) lime+ (5%, 10%, and 15%) fly ash C

![Figure 8](image2.png)  
**Figure 8.** The variations of unconfined compressive strength with different curing times for (5%) lime+ (5%, 10%, and 15%) fly ash C

It is noted that due to the slow lime absorption, the compressive strength of a mixture of soil, lime and volatile ash is slowly developing. Hence, degree of progression of the ‘compressive strength’ of the lime and lime-ash reaction depends on the level of lime uptake by the volatile ash directly, as reported by [18]. The ratio of absorption of the lime is restricted by the level of calcium diffusion through the product reactions. According to [19], It was established that the coarser material is stabilized with lime and fly ash, the higher the volume of volatile ash is needed.

4. Conclusions
In this study, a combination of systematic techniques that were associated to the microstructural features of lime and fly ash treated soil samples were achieved with and without heavy metals. The main objective was to study the morphology behaviour of lime-fly ash treated clay-sand soil contaminated by heavy metals. Firstly, should be mentioned that the use of fly ash and other industrial by-products needs to be intensified to obviate rising the cost of disposal. Thus, due to their pozzolanic properties, can be utilized effectively in a diversity of construction requests.

It was concluded in the current study that the addition of fly ash with the presence of lime led to produce major improvement in the strength properties of the treated soils, thus allowing their reuse in construction applications. Furthermore, it was observed that improving the strength with the presence
of fly-ash is increased with the polymerization time. This has been attributed to the formation of pozzolanic cemented CASH (Gismondine) in the long term. This compound was responsible for the cementations matrix of lime, fly ash, heavy metals and soil, which allowed flocculation and particle interconnections. However, this cemented structure involved adsorbed ions and precipitated metals held as an amorphous mass in pore spaces between flocculated particles. Thus, in cases with heavy metal contamination, adsorption enhanced the strength of treated samples.

Moreover, to evaluate the influence of binder nature based on previous analyses. The interactive behaviours of heavy metals with lime-fly ash are slower than with only fly ash, even though UCS values for lime-fly ash treatment were higher than those obtained from fly ash treatment.

Regarding to the estimation of elemental variation for the treated contaminated soil by Energy Dispersive X-Ray Spectrometry, high levels of crests intensities of Si, Al, and Fe were noticed at all lime-fly ash treated samples. The presence of Iron element was indication on nature of the lateritic soil. Calcium was detected due to the presence of portlandite in fly ash and lime.

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