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1. Introduction

Increasing amounts of residues and waste materials coming from different industrial activities have become a serious problem for the future. However, over the last few years there has been a growing emphasis on the utilization of these materials in several remediation technologies in order to clean up contaminated soil.

Among them, two examples of industrial residues are fly ash and red mud. Fly ash is a by-product of thermal power plants partly used in concrete and cement manufacturing. More than half of it is disposed of in landfills because it finds no other application. It is composed of minerals such as quartz, mullite, subordinately hematite and magnetite, carbon, and a prevalent phase of amorphous aluminosilicate. Red mud is a waste material formed during the production of alumina when the bauxite ore is subject to caustic leaching. It is mainly characterized by the presence of hematite, goethite, gibbsite, rutile and sodium as sodium aluminum silicates or hydro-silicates. A wide variety of organic compounds could also be found (e.g. polybasic and polyhydroxy acids, humic and fulvic acids, carbohydrates, acetic and oxalic acids, furans).

The mineralogical and chemical characterization of these two waste materials is generally carried out by X-ray powder diffraction, thermal analysis, infrared spectroscopy, scanning electron microscopy and chemical methods. Imaging spectroscopy under controlled conditions in laboratory is also applied.

Many research activities on the neutralization of fly ash and red mud materials as well as to solve the problems connected to their disposal are developed in the last few years. Some of these focus on their utilization in different remediation technologies to immobilize toxic elements. They are in fact used in solidification/stabilization technologies for soil remediation treatment and some studies are based on the immobilization of toxic elements in synthetic zeolites crystallized by treated fly ash.

The chapter investigates these two industrial residues focusing both on their chemical-mineralogical properties and their characterization as toxic materials. Studies of remediation methods to reduce the environmental risks due to polluting metals by using red mud and fly ash are presented as well as examples of landfill monitoring and airborne hyperspectral
remote sensing application to analyze red mud soil contamination near urban areas. Significant research activities are being carried out and the aim of this chapter is to show the latest studies underlining the importance of multi-technique application in laboratory and plant scale studies.

2. Fly ash and red mud characterization

2.1 Fly ash
Fly ash is the main combustion by-product from coal-fired power plants and it is partly used in cement manufacturing due to its well-known pozzalonic reactivity (Larosa, 1992). Unfortunately, more than half of fly ash is disposed of in landfills because it finds no other application. The huge production of fly ash is extremely worrying because of this kind of disposal and several investigations have been carried out in order to try to exploit this waste material.

Over the last few years fly ash has been gaining ground in finding solutions to environmental problems and in particular it has being used to the synthesis of zeolites, hydrated aluminosilicate minerals with a three-dimensional open structure making them very useful for solving the mobility of toxic elements in a number of environmental applications. This is due to the mineralogical composition of this waste material.

Fly ash is characterized by quartz, mullite, subordinately hematite and magnetite, carbon, and a prevalent phase of amorphous aluminosilicate (Bayat, 1998; Hall & Livingstone, 2002; Hower et al., 1999; Koukouzas et al., 2006; Kukier et al., 2003; Mishra et al., 2003; Sokol et al., 2000). The abundance of amorphous aluminosilicate glass, which is the prevalent reactive phase, is what makes fly ash an important source material in zeolite synthesis.

Fly ash cannot be properly used, both in cement manufacturing and in environmental application, without an in-depth knowledge of its mineralogical and chemical characteristics. So far there have been lots of publications dealing with the morphological characterization of this material using scanning electron microscopy technique equipped with backscattered and secondary electron detectors and coupled with energy dispersive X-ray spectrometer (SEM-EDS) (Katrinak & Zygarlicke, 1995; Kutchko & Kim, 2006; Sokol et al., 2000; Vassilev et al., 2004). Many studies have been carried out by using the thermal analysis (TG/DTA) (Hill et al., 1998; Li et al., 1997; Machrzkak-Kucbca & Nowak, 2004; Paya et al. 1998; Sarbak & Kramer-Wachowiak, 2001; Szeceényi et al. 1995; Vempati et al. 1994) and the X-ray powder diffraction (XRD) (McCarthy & Solem, 1991; van Roode et al., 1987; Ward & French, 2006) in order to gather compositional information, too. Many works report the use of XRD and Fast Fourier spectroscopy (FTIR) (Vempati et al.1994) in order to identify and quantify glassy materials contained in fly ashes.

Fly ash application is also closely related to its chemical composition. In fact, a large amount of potentially hazardous leachable elements (Brindle & McCarthy, 2006; Jegadeesan et al., 2008; Nakurawa et al., 2007) restricts the application of this material.

2.1.1 Characterization of Italian fly ash samples: a case study
The authors characterized four Italian fly ash samples through a multi-method approach. In order to determine the possible utilization of these materials for concrete and cement manufacturing or for environmental application, also synthesizing zeolite and several morphological, chemical and compositional parameters were thoroughly investigated and compared.
Four coal fly ashes resulting from the combustion of four different coal materials were supplied by ENEL thermoelectric powder plants in Brindisi and Venice – Italy. The particle size distribution was studied by laser granulometry using the principle of laser diffraction. The fly ash samples were also analysed by SEM-EDS. This analysis provided detailed imaging information about the morphology and surface texture of each single particle, as well as the elemental composition of samples.

The chemical abundance of major elements was determined by X-ray fluorescence (XRF) (Franzini et al., 1075; Leoni & Saitta, 1976) and the concentrations of potentially harmful trace were measured by inductively couple plasma spectrometry (ICP-MS) after total acid dissolution treatment of the samples.

The mineral composition of fly ashes was determined by XRD and the quantitative XRD analysis of crystalline phases was carried out by using the reference intensity ratio (RIR) method (Chung, 1974a; 1974b; 1975) combined with the “method of known additions” (Snyder & Bish; 1989). The amount of amorphous materials was calculated through the subtraction of crystalline components. Finally, thermogravimetric analyses were carried out in order to find out the concentration of unburned carbon.

The complete resulting distribution of the particles of fly ash samples are shown in Figure 1. Two samples are mainly made of particles whose diameters range from 5 to 50 µm, the other fly ashes show two main set ranges from 5 to 30 µm and from 70 to 90 µm. All the samples analyzed show an ultra fine fraction ranging from 0.5 to 2.0 µm. This slight variation in size distribution could be due to similar methods for collecting fly ash used in the different power stations.

![Fig. 1. Particle size distribution of the fly ashes samples.](www.intechopen.com)
The morphological study confirms the results on particle distribution and shows that the typical aspect of globules is close to an ideal sphere in shape (Fig. 2).

Fig. 2. SEM images of typical fly ash shape.

The amount of unburned carbon was estimated to be about 6% derived by comparing the results obtained through the thermogravimetric analysis carried out in different environmental atmospheres (Fig. 3). LOI value was calculated by using both flow of inert and oxidising gas (the latter is composed of air and CO2, 1:1). When fly ashes were heated in inert gas, the loss of weight due to the water released from hydrated lime can be estimated because, obviously, in an inert environment, carbon oxidation does not take place. The utilization of an oxidising atmosphere permits the determination of the loss of ignition due to carbon oxidation, plus a water loss from hydrated lime. The first reaction takes place within the range 500-800°C, as showed by a large peak in that range. A comparison between the two values permits the calculation of the amount of unburned carbon more precisely.

The XRD patterns in Figure 4 show that the main crystalline phases are mullite and quartz. The broad hump in the region between 10 and 25 °2θ indicates the abundant presence of glassy phase due to the rapid cooling of fly ash at high temperatures. The weight fractions of mineral and amorphous phases are shown in a diagram (Fig. 5).

The high percentage of amorphous material and the presence of hematite/goethite on trace give evidence of the application of these fly ashes in cement products and zeolite synthesis. The chemical composition for major elements, the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio ranging from 1.7 to 2.0, and the low concentration of toxic elements represent important factors for the application of these materials as well.
Basing on their physical, chemical and mineralogical composition, all the fly ash samples analyzed could be used in cement manufacturing and environmental application.

Fig. 3. Thermogravimetric analysis of fly ashes. TG and DTG curves using inert or oxidising gas.
Fig. 4. X-ray diffraction patterns of each samples of fly ash and relative weight fractions of minerals and amorphous phases. Mul = mullite; Qtz = quartz.

Fig. 5. Weight fractions of minerals and amorphous for each sample of fly ash analyzed.

2.2 Red muds
Red muds are residue alumina products deriving from the Bayer process by the digestion of crushed bauxite in concentrated caustic (NaOH) at elevated temperature. They consist mostly of hematite and goethite together with boehmite, calcium oxides, titanium oxides
and alluminosilicate minerals (e.g. Hanahan et al., 2004; Santona et al., 2006). The chemical analysis generally reveals the presence of Si, Al, Fe, Ca, Ti as well as an array of minor constituents such as Na, K, Cr, Ni, Mn, Cu, Zn and Pb (e.g. Chvedov et al., 2001; Hanahan et al., 2004; Palmert et al., 2007).

Red mud varies in physical, chemical and mineralogical properties due to differing ore sources and refining processes employed and for this reason also this waste material must be deeply characterized before its use for environmental application. The red mud waste risk is mainly due to the accumulative contamination of land and the surrounding dwellings with fine particulate that is highly alkaline and hence needs special precaution to prevent contamination of surrounding natural or urban environments and to avoid consequential exposure and health risk to inhabitants (Mymrin & Vazquez-Voamonde, 2001).

For this kind of studies, the total element composition is usually analyzed by X-ray fluorescence spectroscopy (XRF), whereas the mineral composition is determined by X-ray diffraction (XRD). The samples are also used for examination of micromorphological characteristics by SEM and for thermogravimetric analysis. Few spectroscopic studies are available (Palmer et al., 2007, 2009) including mid-infrared (IR), Raman, near-infrared (NIR), while there is limited report on the red mud optical characterization. Recent literature data also show the utilization of imaging spectroscopy and airborne hyperspectral remote sensing to characterize red mud and mapping the red dust distribution on soils (Pascucci et al., 2009). Furthermore, different studies have highlighted the application of field and imaging spectroscopy for identifying minerals and soils containing pollutants (e.g., heavy metals) as an indicator of contamination in mining areas (Choe et al., 2008; Mars & Crowley, 2003). Kemper and Sommer (2002) in their study have been assessed heavy metal concentrations using reflectance spectroscopy and statistical prediction models recommending the opportunity of applying their technique to remote sensing. In Swayze et al. (2000) the authors describe a procedure and their results attained using imaging spectroscopy to map acidic mine waste. Cécillon et al. (2009) in their work examine critically the suitability of NIR reflectance spectroscopy as a tool for soil quality assessment concluding that (a) imaging NIR enables the direct mapping of some soil properties and soil threats, but that further developments to solve several technological limitations identified are needed before it can be used for soil quality assessment and (b) the robustness of laboratory NIR spectroscopy for soil quality assessment allows its implementation in soil monitoring networks, however, its regular employ requires the development of international soil spectral libraries that should become a priority for soil quality research.

2.2.1 Hyperspectral remote sensing data for mapping red dust: a case study

Techniques for direct identification of materials through the exploitation of spectral features from field and laboratory reflectance spectra have been in use for many years being successfully applied to imaging spectrometer data (Ben-Dor et al., 2009; Clark, 1999; Clark & Roush, 1984; Viscarra-Rossel et al., 2006).

Within this context, the authors have been optically characterized red dust widespread on soils by laboratory and field analyses and used hyperspectral remote sensing data to map its distribution on soils in the surrounding of the impoundment area of an aluminium plant in Montenegro.
In situ spectral analyses were carried out to characterize and separate the red dust optical spectral features and shapes from other soils and backgrounds as well as to construct a spectral library of different materials useful for calibrating and validating the remote sensing data acquired within the study area. At ground reflectance spectra in the 350–2500 nm range were acquired on red mud and red dust widespread on nearby soils using a field portable spectrometer (ASD), from a height of 1 m using a field of view of 25° and a spectalon panel in the same geometry (i.e. at-nadir on the samples) as a white reference to enable directly conversion of the measurement data into reflectance values.

Moreover, several dry red mud samples from the red mud impoundment and soil samples with different concentrations of surfacing red dust were collected for laboratory analyses. The mineral composition of the collected samples was determined by XRD. Pure dried red mud samples and red dust polluted soils were analysed for bulk mineralogy on randomly oriented powders of whole rocks (Srodon et al., 2001). The samples were scanned from 2° to 70° 2θ. The XRD patterns of the pure red mud samples has confirmed the main presence of hematite, goethite, gibbsite and boehmite, rutile and sodium as sodium aluminium silicates or hydrosilicates, and of different red dust polluted soil samples exhibit, instead, the main presence of quartz, phyllosilicates, feldspar and carbonates, and goethite/hematite are also present.

The chemical abundance of major and trace elements (e.g., Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Se and Pb) in the samples were measured using tube excited EDXRF. Using this system, optimum sensitivity for a particular element is achieved having the dual effect of improving sensitivity and reducing background.

Finally, MIVIS hyperspectral airborne remote sensing data collected over the study area were calibrated to radiance and atmospherically and geometrically corrected to obtain reflectances from the Visible to the Short Wave Infrared (0.4-2.5 μm) (Bassani et al., 2006). The reflectance spectral library analysis of the collected red dust samples showed that the dominant spectral features in the VIS-NIR (0.4-1.5) range are primarily related to the iron oxides (hematite - Fe2O3 and/or goethite - Fe3+O(OH)) absorption features. Phyllosilicates (clay minerals) are also largely present in the samples in the form of gibbsite and their strong spectral absorption feature in the SWIR region due to a combination of the O-H stretching fundamental with the Al-O-H bending mode (Clark, 1999) severely influences the SWIR spectral behaviour of the red dust polluted soil samples.

Figure 6 shows an example of reflectance spectra (black line) acquired by ASD spectrometer under controlled conditions in our laboratory on a representative soil sample with a high concentration of red dust on its surface in comparison with the pure USGS spectra (available at: speclab.cr.usgs.gov/spectral-lib.html) of the main minerals constituent of the red dust samples as derived from XRD analysis. This comparison was performed for the each spectrum acquired in the field in order to individuate which mineral constituent primarily influences the red dust spectrum shape and absorption features. Results attained for the analyzed polluted soil samples show that, even on naturally red soils, the red dust deposited from wind is spectrally detectable if a high level of red dust is present on it.

In Figure 7 is presented the map of the red dust distribution on soils as obtained by classifying airborne hyperspectral reflectance data using a simple and fast spectral-shape based algorithm (i.e. the Spectral Feature Fitting procedure, see Segl et al., 2003 and the references therein). The reference soil field spectra in the 0.4-2.5 μm spectral region were scaled to match the image spectra after they were normalized with the continuum removal approach to allow the comparison of individual absorption features using a common
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Fig. 6. Example of a lab ASD reflectance spectra (black line) acquired under controlled conditions on a typical soil sample with high level of red dust (RD) on its surface in comparison with the pure USGS spectra of the main minerals composing the RD samples.

Fig. 7. Location of the study site on a map by UNEP/DEWA/GRID-Europe (2007) showing the hazardous industrial sites, water pollution and mining hot spots in eastern Europe and photos of the investigated site (on the left); red dust map depicted in red over MIVIS band 13 (0.68 μm) (on the right).
baseline. Based on visual field accuracy assessment and laboratory analysis to more quantitatively verify our results, we were able to confirm that the red dust map attained for the chosen study area has reached a good level of accuracy (i.e. an Overall Accuracy of 86%). The attained promising results highlight the usefulness of hyperspectral remote sensing data for mapping hazardous industrial pollutant, such as the red dust deposition on soils, providing their exact position.

3. Solidification/stabilization technologies for soil remediation: use of fly ash and red mud

Over the last few years a great deal of research has been carried out in order to develop remediation methods for reducing environmental risks due to polluting metal and several soil remediation technologies are based on physico-chemical processes of solidification/stabilization (S\S). In general, solidification refers to the physical encapsulation of the contaminant in a solid matrix while stabilization includes chemical reaction to reduce contaminant mobility (Mulligan et al., 2001). The S\S process could be applied both in laboratory and in situ showing good results against the risk with the remarkable benefit of immobilizing heavy metal inside natural minerals, such as clays and zeolite or soil-compatible materials. Among these, fly ash and red muds are widely used (Apak et al., 1998; Castaldi et al., 2010; Ciccu et al., 2003; Coruh & Nur Ergun, 2010; Dermatas & Meng, 2003; Garau et al., 2011; Glenister & Thornber, 1985; Gray et al., 2006; Lombi et al., 2002a; McPharlin et al., 1994; Summers et al., 1996).

In particular, many authors show that amendment of contaminated soil with red mud results in a durable reduction in metal mobility and also in a smaller risk of metal re-mobilization if soil pH were to decrease (Gray et al., 2006; Lombi et al., 2002a). Detailed experiments on the evaluation of the interaction mechanisms between red mud and heavy metals also indicate that only low toxic elements concentration absorbed by red muds are in the water-soluble and exchangeable form while the greatest concentration of metals absorbed are tightly bound and would not be expected to be released readily under natural conditions (Santona et al., 2006).

Application of red mud can also lead to a reduction in heavy metal uptake by plants (Friesl et al., 2003; Lombi et al., 2002b; Muller & Pluquet, 1998).

Other methods for reducing environmental risks lean towards toxic element immobilization using fly ash or zeolite synthesized from fly ash.

The addition of fly ash during S/S treatment of heavy metal contaminated soil is mainly responsible for their effective immobilization by absorbing the waste species on their surfaces or determining precipitation mechanisms (Dermatas & Meng, 2003; Singh & Pant, 2006; Vandecasteele et al., 2002). Precipitation of heavy metals results from the presence of calcium hydroxide, while adsorption may be due to the presence of silica and alumina available in fly ash.

Synthetic zeolite can be added to polluted soils (Querol et al., 2006; Lin et al., 1998; Rayalu et al., 2006) or crystallized directly in those contaminated (Belviso et al. 2010b; 2010c; Terzano et al., 2006) in order to solve environmental problems.

Zeolites are hydrated aluminosilicate minerals with a three-dimensional open structure making them very useful for solving the mobility of toxic elements in a number of environmental applications (Babel and Kurniawan, 2003; Ćurković et al., 1997; de’Gennaro et al., 2003; Inglezakis et al., 2002, 2003; Kesraoui-Ouki et al., 1994; Kocaoba et al., 2007;
Moreno et al., 2001a, 2001b; Ouki and Kavannagh, 1999; Pansini & Colella, 1990; Querol et al., 1999, 2001, 2002; Rayalu et al., 2006; Stefanović et al., 2007; Torracca et al., 1998; Woolard et al., 2000; Wu et al., 2008). All this is strictly connected with their ability to exchange cations, their large surface area, and their typical structural characteristics (such as porosity), which facilitate pollutant absorption and encapsulation.

This mineral can be synthesized from different source materials and fly ash is one of the most used (Bergkaut & Singer, 1996; Querol et al., 2002; Shi & Chang, 1996; Shigemoto et al., 1993). Numerous methods have been suggested for the zeolite synthesis including hydrothermal reaction (Holler & Wirsching, 1985; Murayama et al., 2002; Querol et al., 1995, 1997a; 2001; Shi & Chang, 1996; Tanaka et al., 2003), hydrothermal reaction with a fusion pre-treatment (Bergkaut & Singer, 1996; Chang & Shi, 1998; Rayalu et al., 2000; Shigemoto et al., 1993, 1994), molten-salt methods (Park et al., 2000a; 2000b), methods employing microwaves (Inada et al., 2005; Katsuki et al., 2001; Querol et al., 1997b; Slangen et al., 1997) and ultrasonic treatments (Belviso et al., 2011; Lee et al. 1995; Park et al., 2001; Wang et al., 2008). Distilled water is used in most of the experiments conducted with these different methods, whereas the synthesis of zeolite with seawater is described in very few articles (e.g. Belviso et al., 2009; 2010a; Lee et al., 2001). The authors carried out experiments on zeolite synthesis at low temperature in a soil artificially contaminated with heavy metals (in separate experiments) and treated with fly ash. The role played by this mineral in the immobilization of heavy metals was investigated (Belviso et al. 2010b; c). The results obtained show that the direct synthesis of zeolite takes place readily after a month and the amount of the newly-formed mineral increases during the entire experimentation period. The presence of heavy metal does not exert any influence on zeolite formation which, on the contrary, plays a leading role in the mechanism of the toxic element immobilization. In fact, a reduction in toxic element availability characterizes the soil samples in which zeolite was synthesized. In particular the data about Ni (Belviso et al., 2010b) and Pb suggest that the mobilization of this elements takes place only after zeolite structure is destroyed. This causes the availability of the metals, previously trapped in the mineral and/or co-precipitated on its surfaces in the oxidable and hydroxide form respectively. In all cases synthetic zeolite forms complexes with the toxic metals which are broken by a strong chemical attack but are stable under normal environmental conditions.

4. Conclusion

Soil pollution is a worldwide environmental problem and the current technologies used for remediation are generally very expensive. In this context, the development of low cost remediation methods using various industrial residues which do not alter the physical and chemical properties of soils plays a leading role. This would also reduce waste disposal giving new value to industrial wastes through converting them into industrial by-products. Particularly fly ash and red muds could be cost-effective materials capable of treating a variety of contaminants.

A deeply characterization of this waste materials by multi-technique approach is fundamental for their application. In particular, in this study the application of field and laboratory imaging spectroscopy for identifying and mapping soils containing pollutants, such as red dust, was successfully used in a multi-technique approach for waste material detection and soil quality and remediation strategies assessment.
5. References


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Soil contamination has severely increased over the last decades, mainly due to petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals from industrial wastes and human activities. The critical point regarding contaminated soil monitoring is the intrinsic difficulty in defining fixed monitoring variables and indicators as the establishment of any a priori criterion and threshold for soil quality can be still considered subjective. This book is organized into eight chapters and presents the state-of-the-art and new research highlights in the context of contaminated soil monitoring and remediation strategies, including examples from South America, Europe and Asia. The chapters deal with the following topics:

- Monitoring of dioxin, furan, hydrocarbons and heavy metals level in soils
- Biomarkers for the assessment of soil toxicity
- Use of reflectance spectroscopy for soil contaminants and waste material detection
- Remediation technologies and strategies.

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