CHARACTERIZATION OF PAST METALLURGICAL RESIDUES USING GEOPHYSICAL IMAGING: A CASE STUDY OF DUFERCO SITE (BELGIUM)

Itzel Isunza Manrique[1], David Caterina [1], Marc Dumont [1], Benoît Mignon [2], Antoine Masse[2], Pauline Kessouri[3], Jean Christophe Gourry[3], and Frédéric Nguyen [1]

[1] Urban and Environmental Engineering, University of Liege – Quartier Polytech 1, Allée de la Découverte 9-B52, 4000 Liege, Belgium

[2] Centre Terre et Pierre – Chaussée d'Antoing 55, 7500 Tournai, Belgium

[3] Development of the Risk and Prevention Department (DRP/IGT), French Geological Survey (BRGM) – Av. Claude Guillemin 3, 45060 Orléans, France

ABSTRACT: Ancient metallurgical industries produced large amounts of residues which were typically deposited in heaps or tailings ponds. They were derived from mineral processing and metallurgical treatments that were not as efficient as the extraction processes used nowadays. On one hand, metallurgical wastes could represent a potential source of pollution, being an environmental and sanitary threat even centuries after the end of industrial activities. On the other hand, these residues may still contain valuable ferrous materials, non-ferrous metals and other elements considered as critical raw materials. In this regard, remediation strategies can be improved by integrating the valorization of metallurgical residues and potential resource recovery. To this purpose, it is crucial to have in-depth information about the composition of the metallurgical waste, and spatial information to identify and quantify volumes of these residues. Geophysical methods represent suitable non-invasive technologies for subsurface site characterization, imaging lateral and vertical variations in the physical properties of geological environments including anthropogenic deposits. Complemented with ground truth data from excavations, geophysical imagery can be quantitatively interpreted in terms of material(s) composition and zonation, volume(s) estimation, etc. In this contribution, we present the results of an integrated geophysical investigation carried out in a slag heap of the former iron and steel factory of Duferco, located in Belgium. First, we carried out a geophysical survey in the field with a 3D Electrical Resistivity Tomography (ERT) and Induced Polarization (IP) acquisition. Based on these results, we designed a targeted sampling, i.e., excavation and collection of samples at different locations and depths. In the laboratory, we measured ERT and IP in the samples and compared them with elemental chemical analyses. We investigated correlations between the laboratory data and identified different types of slags or 'categories', i.e., slags richer in Fe, Ca and Si. Then we used a probabilistic approach to classify or predict the categories in the whole domain of field acquisition (where no samples are available). To this aim we used the ERT and IP field data co-located with the samples and the elevation at which these samples were taken. Overall, the combination of geophysical measurements in the field, targeted sampling, geophysical measurements in the laboratory and correlations with chemical analyses, may be promising to quantify the metallic content or materials of interest with a discriminating geophysical signature.

Keywords: mine waste, metallurgical residues, resource recovery, geophysical imaging, uncertainty

1. INTRODUCTION

Europe has a long-lasting mining and metallurgy tradition with activities reported as far back as 5000 years ago (Žibret et al., 2020). Nevertheless, some of the indicators to date these activities are based in the reconstruction of past metal pollution using environmental archives concerning lakes, river and estuarine sediments, coastal marshes, soils, peats, etc. (Martínez Cortizas et al., 2016). Additionally, the long-term contamination in soils is detectable even centuries after the end of mining and metallurgy (Asare & Afriyie, 2021). In this view, new methods and technologies are being developed to target remediation strategies, e.g., decontamination of polluted sites via microbial activity (soils) and chemical precipitation (aqueous media) (Vareda et al., 2019), where in-depth knowledge/characterization of the contaminated environments is crucial to strategize remediation (Asare & Afriyie, 2021).

Nevertheless, metal and minerals are needed for the industry, modern technology and even for the environment (clean technologies). Therefore, some of this materials constitute critical resources due to the high economic importance and supply risks (*Critical Raw Materials*, n.d.). In addition, the recent challenges of the mining industry (e.g., inaccessibility of deposits, increase of low-grade ores, land pressure) advise the need to find alternative stocks of materials in the EU (Žibret et al., 2020). Since the mineral processing and metallurgical treatments were not as efficient as nowadays, metalliferous wastes (dusts, slags, tailing wastes, etc.) may still contain valuable ferrous and non-ferrous metals, rare earth elements and other critical raw materials (Sethurajan et al., 2018). In this context, remediation strategies that decrease the amount of waste and prevent the release of metals into the environment, can also be targeted to resource recovery. Still, as indicated by Žibret et al. (2020), to assess the potential of resource recovery from mine wastes in general, it is important to have in-depth knowledge about their composition and homogeneity, as well as their physical and chemical properties.

Geophysical methods are minimally to non-invasive technologies used to characterize the subsurface of geological and anthropogenic environments, by mapping lateral and vertical variations of physical properties (Environmental and Engineering Geophysical Society). In this contribution we used surface geoelectrical methods, i.e., mapping physical properties from the ground surface. They are non-to-minimally invasive technologies of relative low cost, which can optimize sampling surveys of a conventional characterization, reducing the number of drillings and mitigating the environmental footprint of conventional investigation methods (Nguyen et al., 2018). Finally, when calibrated with ground truth data, geophysical results can be linked to useful information for the management of anthropogenic residues, e.g., waste composition, zonation, volume(s) estimation and more advanced hydrodynamic processes (Dumont et al., 2017; Kessouri et al., 2022; Van De Vijver et al., 2021).

In this contribution, we follow an integrated geophysical methodology to identify and quantify different types of materials in a slag heap composed of coproducts from the former iron and steel factory of Duferco (Walloon, Belgium). We made a 3D ERT and IP acquisition in the field and on the basis of the results, we designed a targeted sampling survey. Then laboratory measurements of ERT and IP were carried out on the samples and the results were compared with chemical elemental analyses. The latter data were used to identify groups of different types of slags or categories, i.e., richer in Fe, Ca and Si. We used a probabilistic approach (Hermans & Irving, 2017; Journel, 2002) to classify the geophysical field data according to three different types of slags, integrating the uncertainty of the category predictions.

The above-mentioned methodology for the investigation of Duferco and the results presented here, are part of the NWE- REGENERATIS project (Interreg NWE- Walloon Region) which promotes the use of decision support tools to valorize, recover and regenerate past metallurgical sites and deposits.

2. SITE DESCRIPTION

The site of Duferco – La Louvière (Wallonia, Belgium) is a former iron factory whose activities date back to 1850 and production of steel was carried out until the end of the 20th century. The factory is composed of several zones (see Fig. 1) where different activities were developed, e.g., coking plant, blast furnaces and tailings. In this contribution we focused on the slag heap, which according to the historical studies it is mainly composed of raw materials and by-products of the iron/steel making activities although heterogeneous waste is likely to be present (e.g., scrap metal, wood, refractories).

In terms of geology, most of the slag heap is underlain by alluvium from the Thiriau stream. These quaternary deposits, which can be up to 8 to 10 meters thick, are composed of alternating sandy and clayey layers with local gravel content. Parts of the slag heap may also lie on the Houiller formation made of shale, sandstone and coal.

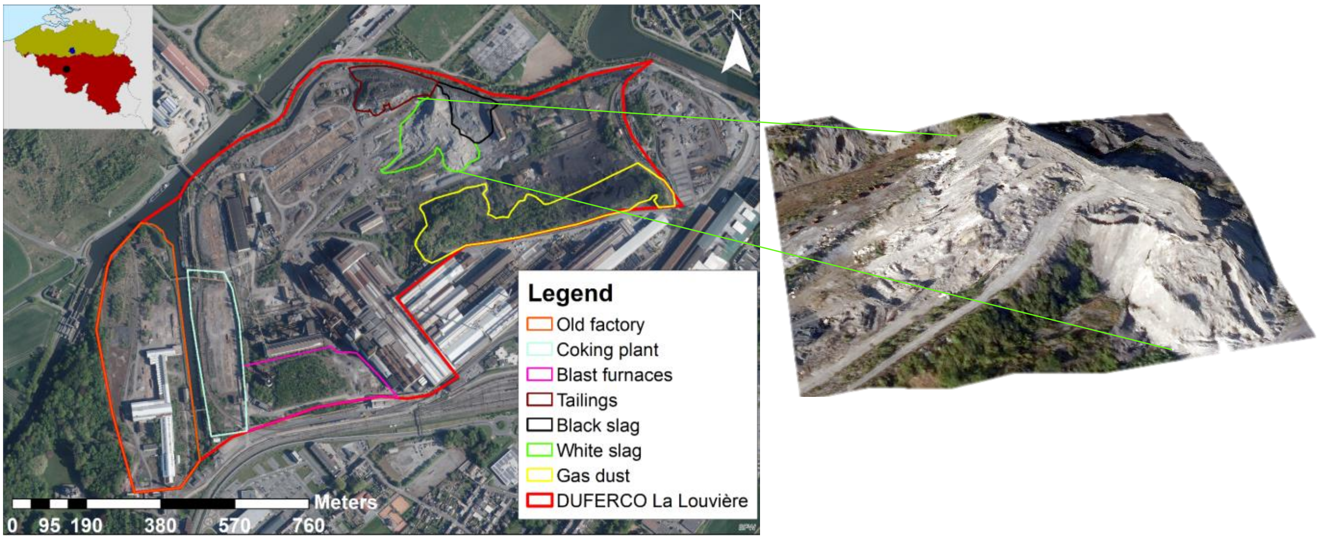

Figure 1. Aerial view of the Duferco site with the delimitation of several activity zones. In this contribution we focused on the slag heap delineated in green solid lines.

3. METHODOLOGY

In the following subsections we explain the integrated methodology we followed to quantitatively interpret geophysical data and characterize the residues of the slag heap. It is based on geophysical field measurements and additionally, it integrates laboratory measurements of geophysical data and chemical analysis. This integrated methodology provides a probabilistic estimation of different types of slags in the whole domain of the field data, allowing to include the uncertainty in the results.

3.1 Geophysical field acquisition and targeted sampling

Time-domain ERT and IP data were acquired with a Terrameter LS system from ABEM. In the white slag heap, 4 2D profiles were deployed, each containing 64 stainless steel electrodes spaced by 2 m. Data acquisition was carried out simultaneously on combinations of two profiles and inline and crossline measurements were collected to obtain a 3D model. For the data acquisition, a gradient array with a ‘s’ factor equals to 7 was used (Dahlin and Zhou 2006). It was complemented with bipole-bipole acquisition. Electrical current was injected for 2 s (delay of 0.8 s and acquisition of 1.2 s) and the voltage decay was measured during 1.86 s after the current was switched off. Measurements were repeated twice to estimate the repetition error and to improve signal quality. A sample of reciprocal measurements was also collected for each profile to assess the quality of data. Data processing of ERT and IP methods lead to 3D resistivity (Ωm) and chargeability (mV/V) models through a data inversion.

Data collected were first filtered by removing all measurements characterized by a repetition error on the measured resistance greater than 5%. Then, in order to weight the data in the inversion process, an error model was calculated on the resistance value using the reciprocal data collected during the acquisition. The absolute error is 2.89E-2 Ω and the relative error 2.27 %. The weighted data were inverted with BERT (Günther et al. 2006) using a robust constraint on the data and a blocky constraint on the model. The 3D models obtained with BERT satisfies the error weighted chi-square, $\chi^2 = 1$ meaning that the data are fitted to their error level.

Finally, on the basis of these results, we designed a sampling survey composed of pits excavations at 8 locations in the slag heap and within the geophysical acquisition domain, and samples were taken at depths of 1,3 and 5 m.

3.2 Geophysical laboratory measurements and chemical analyses

Time-domain ERT and IP laboratory measurements were carried out in the samples, using columns of 1.5 dm^3 (0.08 m ø X 0.3 m) using a Terrameter LS system from ABEM using 4 electrodes similar to a Wenner array. Electrical current was injected for 2 s (delay of 0.8 s and acquisition of 1.2 s) and the voltage decay was measured during 1.86 s after the current was switched off. The same set of samples was analyzed with X-ray fluorescence analyses of major elements such as Fe, Mg, Al and Zn and measured the particle size distribution.

3.3 Correlation between laboratory measurements and chemical analysis

We investigated correlations between the laboratory measurements and chemical analysis. First, we applied a Principal Component Analysis (PCA) using the average content of the elemental chemical analysis. By using the latter elements and the geophysical lab data we identified different types of slags or “categories”: slags richer in Fe, richer in Ca and in Si. Note that in addition to the processes from which the slags were derived (i.e., particular mineralogy/geochemistry), there are several biological and chemical external processes that can affect significantly the slags weathering (Piatak & Ettler, 2021; Yin, 2014).

3.4 Probabilistic classification

Here, we applied a decision analysis based on Bayesian theory, to quantitatively interpret the geophysical field data (Isunza Manrique et al., 2019). We used a probabilistic approach to classify the different types of slags or categories which were identified by the PCA above-mentioned. To build this approach we used the geophysical field data co-located with the position of the samples and the elevations of the slag heap at which the samples were taken.

The probabilistic classification composed of the following steps: 1) definition of categories through chemical analysis and lab measurements, 2) creation of a processing dataset with ERT/IP field values co-located with the sampling and elevation of the samples, 3) estimation of a prior probability of each category, 4) computation of a Gaussian unimodal distributions for the dataset previously formed, 5) computation of conditional probabilities of each category given the dataset from step 2, 6) compute joint conditional probabilities given the dataset using the approximation of permanence of ratios (Journel, 2002). The results of this approach are given in terms of probability models for each category (in the whole field data domain), then we can select the largest probability values to derive a classification model.

4. RESULTS

4.1 ERT and IP field data

Figure 2 shows the final 3D resistivity and chargeability models together with the electrodes position and sampling location. Note that all coordinates are expressed in Belgian Lambert 1972. We use the relative cumulative sensitivity to assess the inverted models, e.g., Caterina et al. (2013). In general, the sensitivity of an inverted model decreases with depth. The cross-sections presented in Fig. 2 include a sensitivity threshold to clip out model cells that might not be reliable.

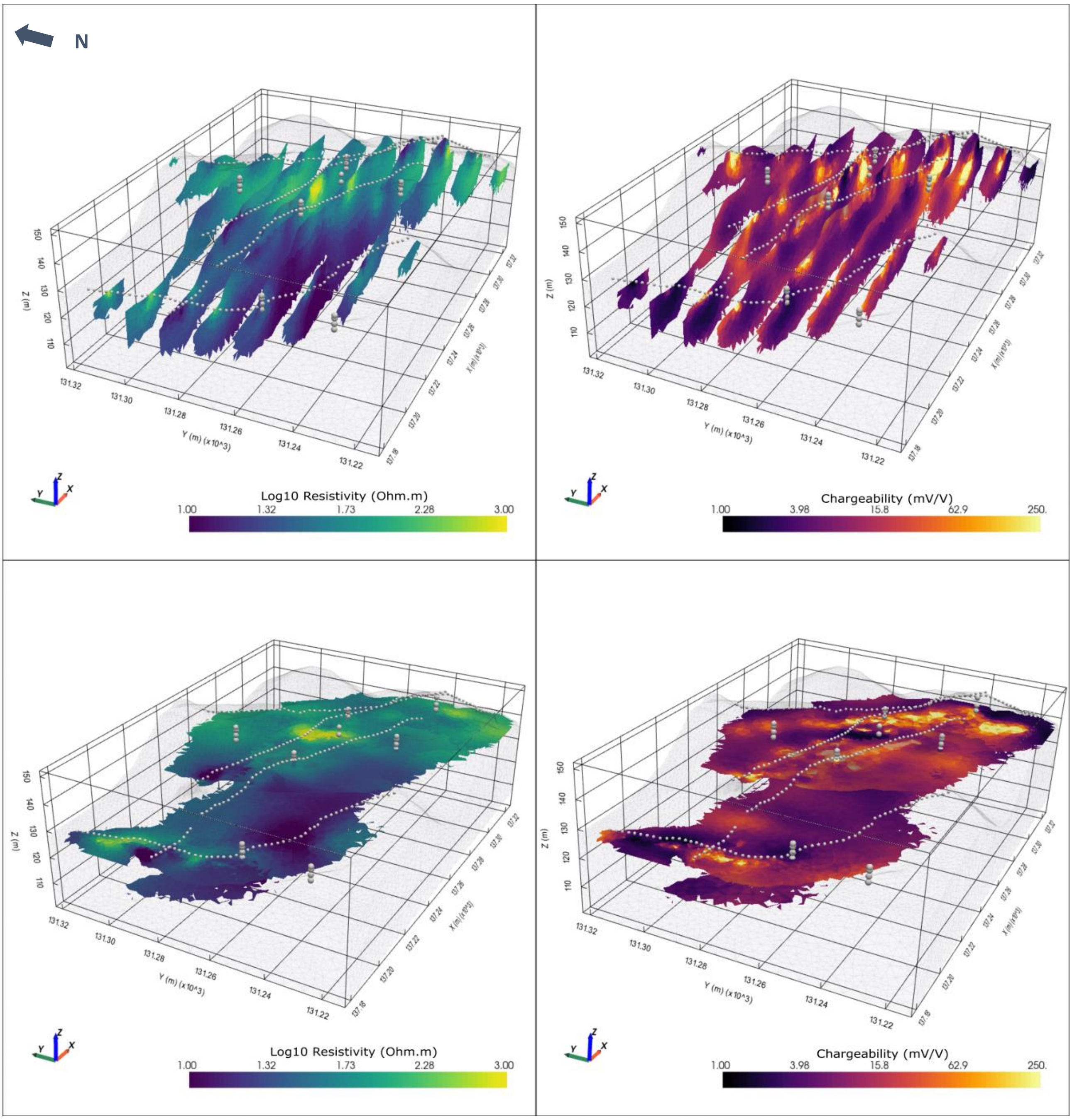

Figure 2. 3D resistivity and chargeability models shown as several cross-sections around the Y axis (top) and around Z (bottom). The electrodes used in the acquisition are shown in the ground surface of the heap as small dots. Large spheres represent the location of the samples. We used PyVista for data visualization (Sullivan &

Kaszynski, 2019).

Overall, we can observe intermediate variations, laterally and vertically in the resistivity model. Yet, the smallest resistivity values are observed close to the ground surface. The chargeability model present stronger contrasts, with the largest values towards the eastern zone and large chargeability values in the central part of the model along a surficial layer. In addition, Figure 2 displays the location where samples were taken. Note that due to logistic reasons drillings could not extend deeper into the subsurface. This means that the calibration of the inverted data is more reliable near the surface as no ground truth data are available at larger depths.

4.2 Correlations between ERT/IP laboratory measurements and chemical analyses

In the PCA we applied in the chemical analysis we obtained that the explained variance ratio was up to 98 % using the average content of Fe, Ca and Si. Thus, we focused in these elements. First, we investigated the coefficient of correlation in linear regressions between the average content of Fe, Ca and Si and the measurements of resistivity (ρ) and chargeability (*C*). Nevertheless, we only obtained an intermediate correlation between the average content of Fe and the chargeability (R = 0.67), observing an increment of chargeability with iron content.

Then, we used the two geophysical datasets in cross-plots together with the average elemental content (see Fig. 3). In this plots we can identify two areas: large resistivity and small chargeability values with a larger Si content and large chargeability values with a higher content of Fe and Ca. Yet, there are no clear zones or ranges of ρ and *C* values which have a larger content of either only Fe or Ca. This means that these geophysical parameters cannot discriminate between a larger content of Fe and a larger content of Ca.

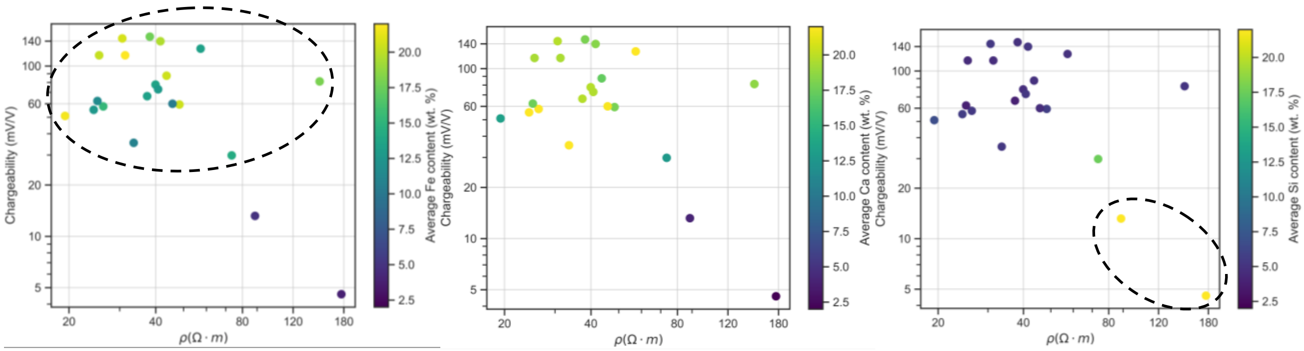

Figure 3. Cross-plots of ρ vs C with colorbar representing the average content of Fe, Ca and Si (wt. %) from left to right respectively. Dashed ellipses indicate the two zones that can be distinguished.

4.3 Probabilistic classification

Figure 4 presents the results of the classification predicted in the whole model domain of the field ERT/IP data. We can observe in general, that slags richer in Fe and richer in Si are highly impacted by large and low values of chargeability respectively. This is in agreement with the cross-plots of Fig. 3, where all the intermediate-to-large chargeability values present the highest average content of Fe while the lowest chargeability is observed in samples richer in Si.

In addition to the field ERT/IP data co-located with the samples, we used the elevation at which the samples were taken in the slag heap. This is a way of including a spatial trend in the probabilistic classification and to better resolve between slags richer in Fe from those slags richer in Ca. Such assumption might be consistent with the successive deposit of metallurgical products during the industrial activity. In addition, the tendency observed in the samples, was that slags richer in Ca were generally found at the largest depths. Therefore, as shown in Figure 4, slags richer in Ca, are predominantly distributed at larger depths in the whole field model. However, this result relies on probability analysis at shallow depths, deeper samples could be needed to ensure the characteristics (resistivity, chargeability, elevation) of each category.

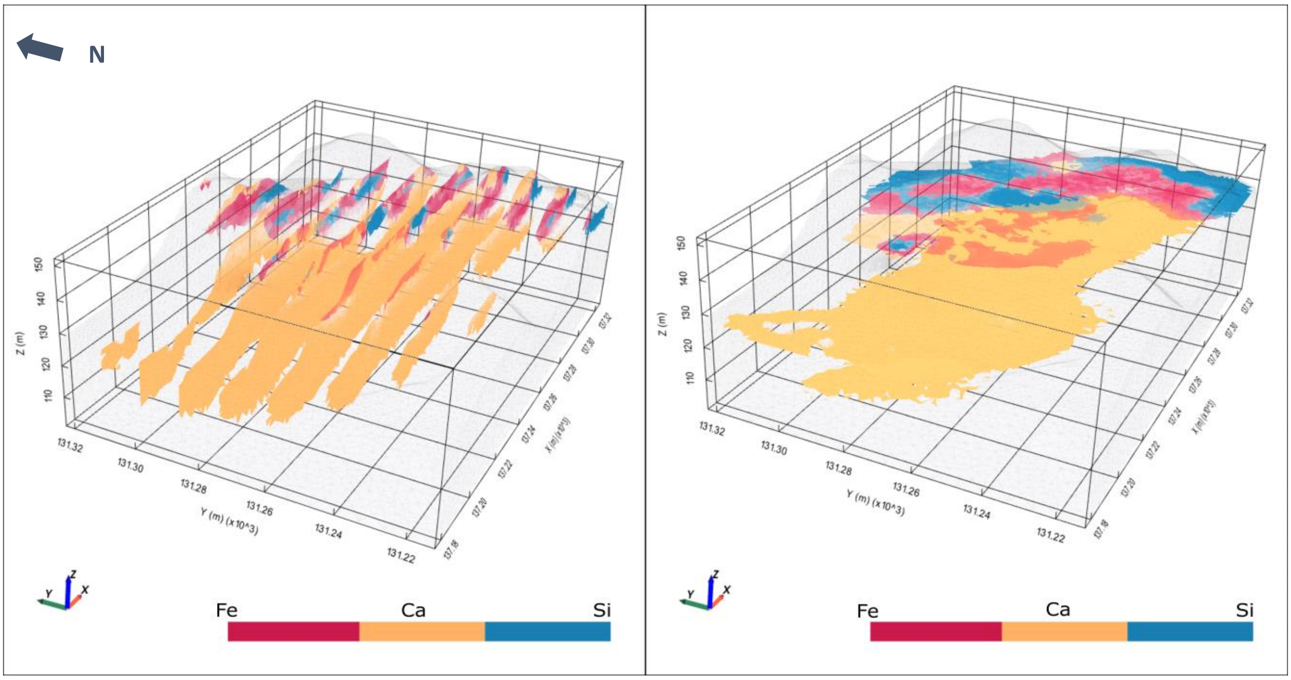

Figure 4. Classification of the field data using the probabilistic approach. Results are shown in several cross-sections around the Y (left) and Z axis (right). Transparencies represent the classification probabilities.

5. CONCLUSIONS

In this work we investigated a slag heap composed of products derived from former iron and steel production. We used an integrated methodology composed of field ERT/IP data, targeted sampling, laboratory ERT/IP measurements and chemical analysis on the samples. We then used a probabilistic approach to classify the field data into different types of slags, richer in Fe, Ca and Si. To build this approach we used the ERT/IP field data co-located with the samples and additionally, the elevations (topography) at which the samples were taken from the slag heap. This probabilistic classification allows to interpret quantitatively the field data and to include uncertainties in the results.

First, the acquisition of ERT and IP data in the field aimed to cover the entire area of the slag heap and thus the spatial resolution might not be small enough to image other types of wastes. This resolution problem is also noted when comparing the field data with the samples which were taken only at shallow depths. In this regard, the probabilistic classification assumes that the composition of the slags observed in the samples are representative of the whole slag heap.

In terms of chemical analysis we observe in general that the slags richer in Fe (and Ca) present the largest chargeability values while the slags richer in Si have the lowest chargeability values. To discriminate between the slags richer in Fe and Ca using the ERT and IP data, a broad chemical analysis may be needed, e.g. in terms of oxides.

The probabilistic approach represent a suitable alternative to interpret quantitatively the field data in spite to the few amount of ground truth data or samples. It allows first, to integrate a prior probabilities or the proportions of the different categories found in the samples, and secondly, to integrate the uncertainty in the prediction of categories in the field data. This approach can be applied in several scenarios and multiple data sets from different sources can be still included.

Finally, the combination of geophysical methods with conventional characterization methods (targeted sampling) together with laboratory measurements and chemical analysis, could be an appropriate methodology to estimate volumes of metallurgical materials of interest with a probability assessment. This information can be used to fill information gaps and improve the management of the site, remediation strategies and the assessment the potential of resource recovery.

ACKNOWLEDGEMENTS

NWE-REGENERATIS project is a multidisciplinary research program financed by Interreg North-West Europe and the Walloon Region which aims to valorize and potentially recover valuable materials while regenerating former metallurgical sites and deposits. We are grateful to Duferco La Louvière (Duferco Group) and all project partners: SPAQuE, OVAM, Bergischer Abfallwirtschaftsverband (BAV), University of Liege, French Geological Survey (BRGM), Materials Processing Institute (MPI), Centre Terre et Pierre (CTP), IXSANE, TEAM2, Technische Hochschule Köln and Cranfield University.

REFERENCES

Asare, M. O., & Afriyie, J. O. (2021). Ancient Mining and Metallurgy as the Origin of Cu, Ag, Pb, Hg, and Zn Contamination in Soils: A Review. *Water, Air, & Soil Pollution*, *232*(6), 240. https://doi.org/10.1007/s11270-021-05166-4

Caterina, D., Beaujean, J., Robert, T., & Nguyen, F. (2013). A comparison study of different image appraisal tools for electrical resistivity tomography. *Near Surface Geophysics*, *11*, 639–657. https://doi.org/10.3997/1873-0604.2013022

Critical raw materials. (n.d.). Retrieved February 14, 2022, from https://ec.europa.eu/growth/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en

Dumont, G., Robert, T., Marck, N., & Nguyen, F. (2017). Assessment of multiple geophysical techniques for the characterization of municipal waste deposit sites. *Journal of Applied Geophysics*, *145*, 74–83. https://doi.org/10.1016/j.jappgeo.2017.07.013

Hermans, T., & Irving, J. (2017). Facies discrimination with ERT using a probabilistic methodology: Effect of sensitivity and regularization. *Near Surface Geophysics*, *15*, 13–25.

Isunza Manrique, I., Caterina, D., Hermans, T., & Nguyen, F. (2019). Probabilistic joint interpretation of geoelectrical and seismic data for landfill characterization. *AGU Fall Meeting, Abstracts*. AGU Fall meeting 2019. http://hdl.handle.net/1854/LU-8639743

Journel, A. G. (2002). Combining knowledge from diverse sources: An alternative to traditional data independence hypotheses. *Mathematical Geology*, *34*(5), 573–596.

Kessouri, P., Johnson, T., Day-Lewis, F. D., Wang, C., Ntarlagiannis, D., & Slater, L. D. (2022). Post-remediation geophysical assessment: Investigating long-term electrical geophysical signatures resulting from bioremediation at a chlorinated solvent contaminated site. *Journal of Environmental Management*, *302*, 113944. https://doi.org/10.1016/j.jenvman.2021.113944

Martínez Cortizas, A., López-Merino, L., Bindler, R., Mighall, T., & Kylander, M. E. (2016). Early atmospheric metal pollution provides evidence for Chalcolithic/Bronze Age mining and metallurgy in Southwestern Europe. *Science of The Total Environment*, *545–546*, 398–406. https://doi.org/10.1016/j.scitotenv.2015.12.078

Nguyen, F., Ghose, R., Isunza Manrique, I., & Dumont, G. (2018). *4TH INTERNATIONAL SYMPOSIUM ON ENHANCED LANDFILL MINING - MANAGING PAST LANDFILLS FOR FUTURE SITE DEVELOPMENT: A REVIEW OF THE CONTRIBUTION OF GEOPHYSICAL METHODS*. 12.

Piatak, N. M., & Ettler, V. (2021). *Metallurgical Slags: Environmental Geochemistry and Resource Potential*. Royal Society of Chemistry.

Sethurajan, M., van Hullebusch, E. D., & Nancharaiah, Y. V. (2018). Biotechnology in the management and resource recovery from metal bearing solid wastes: Recent advances. *Journal of Environmental Management*, *211*, 138–153. https://doi.org/10.1016/j.jenvman.2018.01.035

Sullivan, C., & Kaszynski, A. (2019). PyVista: 3D plotting and mesh analysis through a streamlined interface for the Visualization Toolkit (VTK). *Journal of Open Source Software*, *4*(37), 1450.

https://doi.org/10.21105/joss.01450

Van De Vijver, E., Isunza Manrique, I., Bobe, C., Caterina, D., Hermans, T., Wille, E., & Nguyen, F. (2021, October 30). *Geophysics in support of dynamic landfill management: Moving beyond the challenges*. SEG/AAPG/SEPM First International Meeting for Applied Geoscience & Energy. https://doi.org/10.1190/segam2021-3594435.1

Vareda, J. P., Valente, A. J. M., & Durães, L. (2019). Assessment of heavy metal pollution from anthropogenic activities and remediation strategies: A review. *Journal of Environmental Management*, *246*, 101–118. https://doi.org/10.1016/j.jenvman.2019.05.126

Yin, N. H. (2014). *Weathering of metallurgical slags: A comprehensive study on the importance of chemical and biological contributions*.

Žibret, G., Lemiere, B., Mendez, A.-M., Cormio, C., Sinnett, D., Cleall, P., Szabó, K., & Carvalho, M. T. (2020). National Mineral Waste Databases as an Information Source for Assessing Material Recovery Potential from Mine Waste, Tailings and Metallurgical Waste. *Minerals*, *10*(5), 446. https://doi.org/10.3390/min10050446