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Valorification of Ferroalloy Slag Waste for Environmental Protection

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Abstract: *One of the major problems today in the steel industry is the production of large amounts of waste. The current study aims to present possible ways of recycling and re-use of silico-manganese slag landfilled in Tulcea, City on the Danube River at borders of the Danube Delta Biosphere Reserve to minimize its environmental impact. In the last three decades, the ferroalloy production plant has for over 2.6 million tons of slag. Slag dumps constitute a significant source of air, water and soil pollution who adversely affects the environment and the human health. Landslides are among the many natural disasters causing massive destructions and loss of lives across the globe. The sliding process includes three phases: preparatory, slow, incipient slip phase (foreground processes); the actual slip (crossing the geomorphological threshold) and natural stabilization (balancing, post-threshold processes). Particularly, in Romania, landslides are quite widespread. The motivation of our research is to confirm that exist the possibility to valorificate ferroalloy waste slag to decommissioning of the slag dump by using as aggregate sources to prevent landslides. The proposed research is in concordance with the sustainable use of natural resources for achieve of sustainable development of 2030 AGENDA and Waste Management Legislation, due of the ecological costs are huge on non-conforming waste dump.*

Keywords: *waste slag, pollution, environment*

1. Introduction

Steel industry both in Europe and globally produces large amounts of waste that are dumped in landfill sites. The recycling of these wastes into useful resources is a priority in the EU program Green Deal 2050. The waste produce from steel plants is in the form of slags, sludges, and dust. According with medical researchers the dust particles can cause cardiovascular and respiratory health problems [1-3]. In order to combat these types of health problems and to increase global sustainability is the valorification of a large volume of slag waste dumped in landfill sites [4]. Recently, re-use of different metallurgical slags has attracted the attention of many scientists. Submerged electric furnaces are used in the production of ferroalloys smelted and small number of operations is using blast furnaces or converters. During the ferroalloy production, one ton of slag waste is generated per every three tons of ferroalloy produced and a large amount of slag is landfilled [5]. A small proportion of ferroalloy slag is recycled and treated for application in cement mixture, inner plant recycling, and as armour stones. Disposal of these ferroalloy slags pollute the atmosphere, underground water, and soil, but also need large landfill area. The ferroalloy plant produces ferroalloys of silicon, manganese, chromium, silicon metal and special ferroalloys. The chemical composition of the ferrochrome slag contains in proportion of about 85% of the slag compositions the oxides SiO_2, MgO and Al_2O_3. The domain suitable for ferrochrome slag according with its physical properties is road construction [6]. In the case of low MnO slags the contents of CaO and Fe_2O_3 are low and high in SiO_2, Al_2O_3, MnO, MgO, Na_2O and K_2O. One of the utilizations of the granulated slags is in making blended slag cement with ordinary Portland cement (OPC) and in the case of air-cooled lumpy slag is as aggregate in concrete [7]. Nowadays, a challenging task is to explore the high potential of using slags to replace those products which are competitive in the market. The slags can have the applications in most of the fields, especially in civil engineering because they have a similarity to natural stones. One of the issues in increasing the re-utilization of the slags it is necessary to modify the slag properties by applying suitable heat treatment and by introducing additives. Besides the physical-chemical properties of the slag, there is an increasing demand for more environmental information. Product development must be closely linked to environmental research in order to develop appropriate technology to ensure the quality of slag-containing products in order to promote their use. In recent research, we studied about the re-use of slag with application in industrial sector with material and environmental benefits [8].

Landslides are considered through the many natural disasters which causes massive destructions and loss of lives across the earth. The sliding process includes three phases: preparatory, slow, incipient slip phase (foreground processes); the actual slip (crossing the geomorphological threshold) and natural stabilization (balancing, post-threshold processes). Particularly, in Romania, landslides are quite widespread. The total surface subject to landslides is rated at 900,000 hectares. The most important and well-known landslide was the displacement of the Suhardelului Peak, which led to the dam of the Bicaz River and the formation of the Red Lake. In 1971, the Certej disaster was caused by the rupture of the dam and the landslide of the tailing's mountain from the Certej mining tailings pond, Hunedoara. The tidal wave swallowed up in a quarter of an hour and wiped out six blocks of flats with 25 apartments each, a 30-room home, seven single-family homes and 24 homes that were destroyed or damaged. The disaster killed 89 people and injured 76 others. Other large landslides occurred at Malul cu Flori in June 1979 and Vârfuri in February 1980 - both in Dâmbovița County; Zameş (in 1992) in Bacău County and Izvoarele (August 1993) in Galaţi County. The first 3 cases were triggered by heavy rainfall. If the landslides from Malul cu Flori do not have big losses, the displacement of the land from Varfuri affected the civic center of the locality. 110 houses were destroyed, 21 were severely damaged, and 25 hectares of land and some roads were severely damaged. Landslides have also occurred in the recent past, especially as a result of natural phenomena (heavy rainfall, freezing-thawing, groundwater pressure, etc.), the most recent, heavily publicized, occurred on dated April 10, 2020 in the locality of Azuga (Prahova) [9].

The aim of this present research is to give a usage of the ferroalloy slag waste based on the detailed information collection and landslide surveying and mapping for similar landslide hazard prediction and prevention.

2. Area description

The largest ferroalloy production from East Europe is in S-E of Romania. In Romania is only one ferroalloy plant with a surface area of 65 ha and a production of 1000000 t of ferroalloy / year such as ferroalloy of manganese, silicon, chromium, silicon metal and special ferroalloy. This ferroalloy plant has supplied for about 70% of the necessities of Romanian siderurgy. In the past, the ferroalloy production plant has filled approximately 2.6 million tons of waste slag. The dump is situated in Tulcea, which is the principal city of the county of the same name, Dobrogea, Romania, on the borders the Danube Delta Biosphere Reserve and on the shores of Lake Somova, as can be seen in Figure 1. The Danube Delta Biosphere Reserve is recognized from UNESCO`s Man and Biosphere Program as a wetland of international importance since 1991, especially as a habitat for waterfowl and under the Ramsar Convention, with the Ukrainian Danube Biosphere Reserve is included in the International Network of Transborder Biosphere Reserve since 1999.

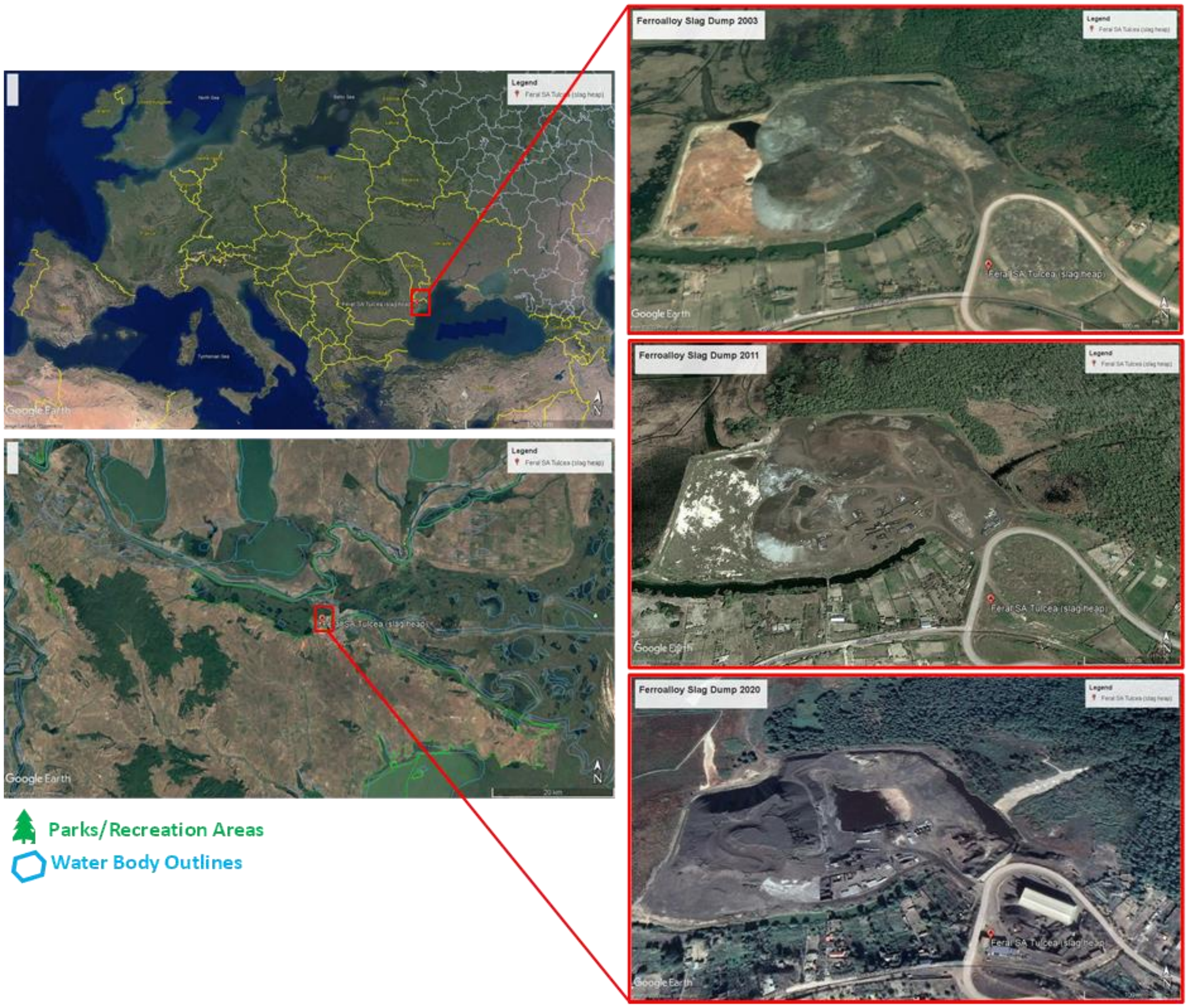

Fig. 1: Map of the sampling site location.

As can be observe in Figure 1, images done with Google Earth, the evolution of the dump since 2003 until 2020 and the increase of the large amount of ferroalloy waste slag dumped in landfill with negative effects on the environment. In in the left picture in can be seen the parks and recreation areas with green line and the water body outlines with blue line on the borders of the dump area.

3. Valorification of Ferroalloy Slag Waste

For a quantitative determination of major and trace element concentrations in solid waste material using a calibration with matrix-matched standards the ferroalloy slag waste was characterized by X-ray Fluorescence (XRF). The chemical composition of the waste slag is presented in Table 1. From the results one we can notice that the main oxides are consisting in silica, magnesium oxide and in small percentage alumina, calcium oxide and potassium oxide.

Table 1: Chemical composition determined with XRF (wt%) of the waste slag.

Element/Oxide	Percentage
Si / SiO_2	20.74 / 44.44
Mn / MnO	24.26 / 31.33
Al / Al_2O_3	3.36 / 6.36
Ca / CaO	4.02 / 5.63
K / K_2O	3.87 / 4.67
Fe / Fe_2O_3	1.55 / 2.21
Mg / MgO	1.28 / 2.12
Na / Na_2O	0.74 / 1.00
Ba / BaO	0.81 / 0.90
S / SO_3	0.17 / 0.42
Zn / ZnO	0.26 / 0.32
Ti / TiO_2	0.12 / 0.21
Cr / Cr_2O_3	0.11 / 0.16
P / P_2O_5	0.05 / 0.09
As / As_2O_3	0.05 / 0.07
Pb / PbO	0.05 / 0.06
Cu / CuO	0.01/ 0.01

Landslides are a major hazard in most mountainous and hilly regions, as well as in coastal areas or riverbanks. Their impact largely depends on the size and their speed, the elements at risk and the vulnerability of these elements. Every year, landslides cause deaths and cause severe damage to infrastructure (roads, railways, pipelines, artificial reservoirs, etc.) and property (buildings, agricultural land, etc.). Under the current economic circumstances, the number of landslides areas that require rehabilitation has grown [10]. Therefore, rehabilitating landslides areas in an environmentally sustainable and cost-effective manner is an engineering challenge [11]. Typically, landslides require a relatively low-strength material compared to other civil engineering structures. Landslides most often occur in areas where the soil is made of different types of clay (clay has the property of swelling during periods of heavy rainfall). Also, the most frequent landslides occur in spring and autumn, when the snow melts, but also when the amount of precipitation is higher. It is very important to mention that landslides are a major threat to human life and have devastating effects on construction, but also on the environment. But more serious is the fact that the importance given to these phenomena is incredibly low, especially if their production does not manifest itself obviously and with an increased speed.

In this study, we propose the re-use of ferroalloy slag waste in areas with landslides. In Figure 2 is presented the map of Romania with the areas which are predisposed to the landslides. The most affected areas are Prahova, Buzau and Vrancea which are at about 300 kilometres distance from slag dump. In present, crushed ferroalloy slag aggregate (FeSiMn and FeCr) is used in roads, foundations, concrete (good replacement of classical aggregates).

It is well known that over 95% of the commercial use of silicon oxide, silica (SiO_2) is in the construction industry, e.g., for concrete production. From the XRF analysis, it can be seen that the most important compound in slag waste is SiO_2, which indicates the use of slag as an additional cementitious material in areas at risk of landslides.

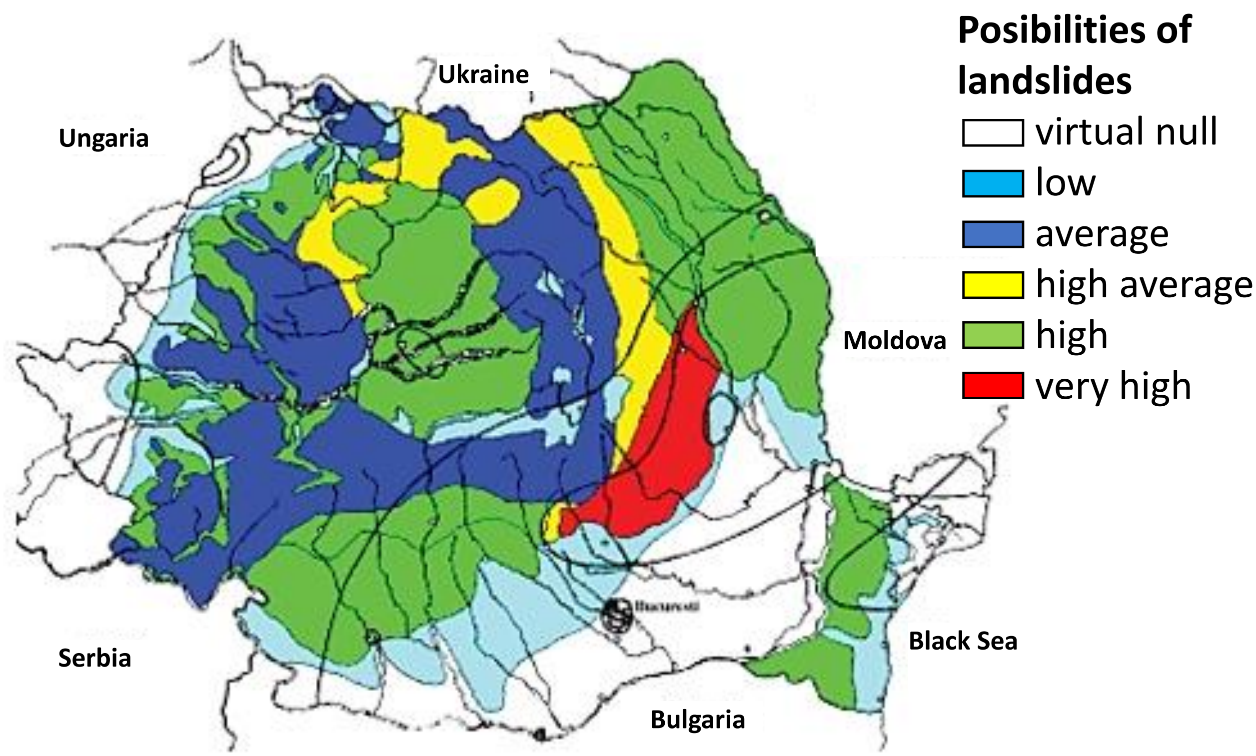

Fig. 2: Map of the Romania country [9]

Moreover, as can be seen from the Map of Romania (Figure 2), the entire eastern part, some areas in the centre, but also the southern part of Romania are exposed to a high landslide hazard, being close to the epicentre, according to the report "National Disaster Risk Assessment (RO-RISK)", published by the General Inspectorate for Emergency Situations (IGSU, 2016). Thus, according to the specialists, the most exposed cities would be those located on the northeast direction: Focsani, Galati, Bacau, Vaslui and Iasi, as well as those located on the southwest direction: Buzau, Ramnicu Sarat, Ploiesti, Bucharest, Targoviste, Pitesti, even Giurgiu and Alexandria.

4. Conclusions

Since 2003 until 2020 was observed the increase of the large amount of ferroalloy waste slag dumped in landfill with negative effects on the environment. Every year, landslides cause deaths and cause severe damage to infrastructure. Therefore, an engineering challenge from an environmentally sustainable and cost-effective manner is the rehabilitating landslides areas.

In this research study, we proposed in situ cementitious rehabilitation using waste slag dumped in landfill from two points of view, namely is considered a cheaper and potentially environmentally sustainable solution because it recycles existing waste materials. Therefore, the ferroalloy slag waste can be used as prime materials for rehabilitation of landslides areas should be cleverly engineered as a potential environmentally and structurally sustainable solution.

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