RAW MATERIAL FOR POWDER METALLURGY OBTAINED FROM ENVIRONMENTAL IRON HYDROXIDES

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Abstract
Iron hydroxides (e.g. goethite and lepidocrocite) are the lower degradation state of iron. The environmental research performed in Cluj – Napoca found large amounts of iron hydroxides in the urban dust and in the nonskid material. The ferrous particles were found in a wide dimensional range, from 20 μm upwards, mixed together with quartz particles. Two paths of magnetic separation were followed: dry separation and wet separation. The iron hydroxide particles were ground for a better dispersion and were subjected to magnetic separation. Two paths of magnetic separation were followed: dry separation and wet separation. Finally, results indicate that wet magnetic separation provides iron hydroxide powder suitable as a raw material for powder metallurgy applications (such as barium ferrite sintered permanent magnet production), as well as reduces the environmental pollution risk.

Keywords: raw material, environmental technologies, iron hydroxides

INTRODUCTION
Modern civilization, developed towards big cities, involves many ferrous materials exposed to the natural environment. Such materials are subjected to weathering corrosion forming a most altered iron compound - iron hydroxide [1 - 4]. Two allotropic forms are known for iron hydroxide: goethite - α iron hydroxide and lepidocrocite - γ iron hydroxide [5, 6]. Both forms of iron hydroxide (rust) are formed on car and lorry chasses even when anti-corrosion protection has been applied to the vehicle (standard manufacturing procedure) [7, 8].

Moreover, some of recent studies point out the presence of iron hydroxides in street dust [8, 9] along with quartz, clay, and other particles which are highly dangerous to the health of citizens [10, 11]. The Regional Environmental Protection Agency Cluj-Napoca (on E.U. Project for Air Parameters Monitoring) found during the 2010 – 2011 winter large amounts of particulate matters in lower atmospheric strata containing significant ferro-hydroxides. The source of these particles was traced to the nonskid materials applied on the streets and roads as rich ferro – hydroxide particles (e.g. goethite and lepidocrocite).

The challenge of present research consists in establishing some technical solution in order to diminish the proliferation of the environmental iron hydroxides to the benefit of metallurgical industry and especially for powder metallurgy. The magnetic separation of ferrous particles is a common procedure for iron ore enrichment, but it is a difficult matter...
for the micro scaled dispersions such as the ferro – hydroxides present in street dusts and even in the nonskid material.

Some researchers applied liquid magnetic separation for the finest ferromagnetic clays such as illite, biotite and even chlorite with significant amount of goethite and lepidocrocite [12, 13]. Used were electromagnetic grids which retain smallest ferromagnetic particles from a liquid stream [12]. The present research is focused on another liquid magnetic separation technical variant using magnetic rods.

EXPERIMENTAL PROCEDURE

The nonskid material (NSM) samples were collected weekly from 5 different points in Cluj – Napoca City, Romania from December 2010 to February 2011. The collected samples were mixed together for uniformity, obtaining a characteristic average sample. The FOP particles (containing high amount of ferro – hydroxides particles) were separated from a representative lot of NSM samples according to their morphology, colour and texture (irregular to round shape, reddish brown colour and friable texture). Both NSM and FOP samples were ground individually in a mechanical mortar to a micro-scaled powder state in order to perform primary analysis and further experiments regarding FOP particles.

The dry magnetic separation was performed on a laboratory magnetic sorter using a 0.5 T magnetic field and the thinnest possibly particle film for a better dispersion of the particles. The wet magnetic separation was performed in a 96% ethylic alcohol in a glass container under mechanical agitation by immersion of magnetic rods (each exhibiting 0.5 T magnetic field) covered with a thin PET foil. After rods’ extraction from the separation tank, the PET foil was removed and dried and resulting powder collected in a special container.

X – ray diffraction was carried out with a DRON 3 diffractometer equipped with a Matmec VI.0 registration and processing software. A Cu kα monochrome radiation was used. A wide range of 2θ angle was used (20° – 100°) in order to find all kind of compounds in the investigated sample. The identification of compounds in NSM and FOP samples was performed using the MATCH standard database from Crystal Impact Company [14].

The microscopic inspection was performed on a Laboval 2 (Carl Zeiss Jena) optical mineralogical microscope in transmitted light and transmitted cross polarized light. The digital capture of microphotographs was done with a Samsung 8 Mpx camera.

RESULTS AND DISCUSSION

The X – ray pattern resulting for NSM sample is presented in Fig.1a. It features very well developed peaks corresponding to a crystalline state of the sample. There were found large amounts of quartz – α SiO₂, lepidocrocite – FeO(OH), goethite – Fe₃O(OH), halite NaCl, and some traces of tridimite – γ SiO₂.

The morphology of initial nonskid material is presented in Fig.2a. The quartz particles appear with rounded shapes, having white to grey colour, halite appears as squared translucent particles, meanwhile FOP particles appear reddish brown [15], the traces of tridimite features some darken rounded particles. The initial nonskid material particle diameter range is situated between 5 and 10 mm. Quartz, even tridimite, particles have the functional role of increasing the road adherence and halite is meant to decrease the water freezing point in winter traffic conditions. Only FOP particles, evidenced by macroscopic characteristics and confirmed by X-ray pattern in Fig.1a, do not have any functional role in
nonskid material. Most likely the FOP particles in nonskid material are environmental iron hydroxides via iron chassis rust, because of the recirculation of the used NSM material.

![X-ray patterns](image)

**Fig.1.** The X–ray patterns for: a) NSM sample and b) FOP sample.

![Morphology and mineral distribution](image)

**Fig.2.** The morphology and mineral distribution in primary samples: a) NSM, b) NSM in cross polarized light, c) FOP in cross polarized light, and d) high magnification of FOP in cross polarized light.

The relative intensities of lepidocrocite and goethite peaks in NSM X-ray pattern indicates an average content of 20 wt.%, in good agreement with macroscopic observations in Fig.2a. Furthermore, this fact is better observed in NSM cross polarized light microphotograph. There appears a large amount of sharp broken quartz particles, due to the grinding of NSM, featuring a green – grey colour with various intensities according to the
particle’s position related to the microscope optical axis. Halite appears as microscopic squared particles with blue light shading. Observed are also large amounts of micro-scaled FOP particles corresponding to the average content of 20 wt.%. 

The X-ray pattern for FOP sample is presented in Fig.1b. It features well-developed peaks corresponding to the crystalline state of the sample. The minerals found in the FOP sample are quartz, lepidocrocite and goethite. The amount of ferro-hydroxides in FOP sample is estimated to be over 60% against quartz, considering the relative intensities of diffraction peaks related to the crystal structure factor. The microstructure of FOP sample, Fig.2c, proves the estimation based on the relative intensities of the X-ray diffraction pattern. There appear a wide range of FOP particles from several μm to over 300 μm diameter having a dark reddish brown colour, mixed with several quartz particles with an average diameter of 70 μm. More refined goethite and lepidocrocite particles in the FOP sample can be observed at high magnification in Fig.2d. The smallest ferro-hydroxide particles in FOP samples have a range from 20 to 100 μm, featuring a bright reddish brown colour. There is no quartz particle in Fig.2d. The observed microstructure for the FOP sample allows us to assume that a proper magnetic sorting will provide a ferro-hydroxide powder free of impurities such as quartz.

The dry magnetic sorting of the FOP sample assures an extraction coefficient of 31.74 wt.%, which is a very good one. The risen question is about the purity of the dry sorted powder. The X-ray diffraction analysis performed on the resulting powder shows a greater amount of ferro-hydroxides, but still detects quartz in the structure, Fig.3a.

![Fig.3. X-ray diffraction patterns for the FOP particles resulting from a) dry magnetic selection and b) wet magnetic selection.](image)

The microstructure of dry magnetic selected powder, Fig.4a, presents well individualized lepidocrocite and goethite particles, around 40 μm in size, and several quartz and trydimite particles in a close dimensional range of 35 μm. The cohesion between small micro-sized particles is a setback for realizing high purity by the dry magnetic separation.
Despite quartz particles embedded among ferro-hydroxide particles, we found some micro areas without impurities; such high magnification detail is presented in Fig.4b.

We propose a technical method which allows floating of individual micro particles. The 96% ethyl alcohol fulfils all the requirements for a proper defloculation of the FOP sample in conditions of mechanical agitation. A powder / liquid ratio of 1 kg/l was used in order to achieve the proposed goals. Thus, the larger quartz particles will be subjected to an almost immediate sedimentation to the bottom of separation tank; meanwhile smallest goethite and lepidocrocite particles will be floating in the dispersion.

The magnetic rods are immersed at the top of the separation tank allowing ferro-hydroxide micro particles to stick on their surfaces. The powder resulting after wet magnetic separation sustains an extraction coefficient of 6.2 wt.%, significantly lower than the value obtained by dry magnetic separation. However, the main goal is to obtain a better purity of resulting ferro-hydroxide powder.

The wet separated FOP sample was investigated also by X-ray diffraction, resulting in the pattern in Fig.3b. We notice that goethite and lepidocrocite are the only minerals detected. It means that the quartz amounts are below the diffractometer sensitivity (< 1%). The high purity of wet magnetic selected powder is observed also in Figure 4c where the lepidocrocite and goethite mixture appears intense red on dark background. The high magnification image, Fig.4d, reveals the morphology of resulted ferro-hydroxide particles derived from ideal acicular shapes having an average diameter of 15 μm, corresponding to a high grade of uniformity. We notice in Fig.4d that the quartz particles are missing, proving the success of the wet magnetic selection.

The iron hydroxide powder resulting from wet magnetic separation seems to be uniform, having an average size of 15 μm, which could be suitable for powder metallurgy application, as resulting, or could be subjected to hydrogen reduction to achieve iron powder. However, the presented wet separation technical method could be improved as an
environmental source of powder metallurgy raw material for different processes such as the fabrication of barium ferrite sintered permanent magnets [16, 17]. A more detailed analysis of the traces in the achieved raw material is the subject of a further article concerning this research, in order to fit the specific powder metallurgy process.

The total amount of NSM involved in the winter season in Cluj Napoca City is situated around a few hundred tons, similar to other large cities. The extraction percent of 6.2% assured by wet magnetic separation allows extraction of a significant amount of raw material. It could be suitable for a small environmental powder metallurgy factory oriented to barium ferrite permanent magnets production.

CONCLUSIONS
The performed research on the environmental iron hydroxides proves that the nonskid material sample collected during December 2010 – February 2011 contains significant amount of iron hydroxides (goethite and lepidocrocite) situated around 20 wt.%. Such amounts could be very dangerous for human health. The magnetic separation applied to the FOP samples reveals interesting aspects favourable to an environmental improvement. The dry magnetic separation achieves a high extraction coefficient (31.74%) related to a lower purity of the resulting iron hydroxide powder. The wet magnetic separation assures a high purity of resulting powder, which could be suitable for a powder metallurgy application, related to a low extraction coefficient (6.2 wt.%). The achieved extraction coefficient related to the high amount of NSM used in winter season in large cities could be suitable for a small environmental powder metallurgy factory. The basic technical solution for wet magnetic separation could be improved to increase the extraction coefficient by a more adequate design suitable for the observed particles involved in the separation process.

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