XI Naučno/stručni simpozij sa međunarodnim učešćem
„METALNI I NEMETALNI MATERIJALI“ Zenica, BiH, 21-22. april 2016.

MINING HOTSPOTS-POTENTIAL IN EXPANDING THE CHEMICAL AND PHYSICAL APPLICATIONS OF NANOMATERIALS

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Key words: mining sludge, recycle, nanotechnology, nanometalic materials

RESUME
Nanometalic materials are at the present moment the most commercialized class of nanomaterials. Methods for their synthesis and exploitation of the physical phenomena of their behaviour on atomic level are ever-expanding. Their prices are sometimes too high and in lowering the price, finding the new recourses of raw materials, would be crucial. Recent results in research on mining hotspots, in particular the accumulation lakes for waste water coming from the ore washing process are very promising. It is indeed possible to extract the wasted metal from the sludge at the hotspots, convert it into the concentrated metal ionic solutions and then prepare the high-quality nanometalic particles. These could than have very attractive applications from catalysis, optics, solar cells and memory devices to even medicine if purified enough. The newest findings in this area will be discussed, together with the potential of numerous mining hotspots along Bosnia and Herzegovina and Europe as a whole.

1. INTRODUCTION

The history of mining has more or less defined human development with even the eras called upon the metal or the alloys which were discovered at that time metal application induced huge steps in improvement of human life. Today the history writes about the copper age, bronze age etc. The chronology of the inventions in the metal processing area can be found widely documented in archaeological literature with most authors [1, 2] agreeing on the following order:
(1) Gold (ca) 6000BC - Stone Age man making gold jewellery.
(2) Copper, (ca) 4200BC - The use of copper was more significant than gold as the first tools, implements and weapons were made from copper.
(3) Silver, (ca) 4000BC - Silver was widely used throughout the history as a basis for monetary systems of the Roman and Chinese Empires.

(4) Lead, (ca) 3500BC - It is possible that lead smelting began at least 9,000 years ago.
(5) Tin, (ca) 1750BC - First smelted in combination with copper around 3500 BC to produce bronze.
(6) Iron, smelted, (ca) 1500BC - The discovery of smelting around 3000 BC led to the start of the Iron Age around 1200 BC with wide use of iron for tools and weapons.

However, the rapid development of the mining technologies inevitably is heading the human race to the depletion of the mining recourses at least these which are available in the high parts of the Earth crust and which can be relatively safely exploited. The recycle of the metal waste (parts of the machines, construction garbage, everyday house garbage etc.) is, of course developing also rapidly, but sometimes is complicated by lack of the country recycling policies. Also, there are technical troubles such as too many ingredients in the alloy which makes their separation expensive or even impossible. Therefore, an obvious choice for increasing the effectiveness of mining exploitation would be to research more about the mining waste. However, not much has been done in this area.
This paper will discuss the potential application of the metal mining waste from the lake accumulations in nanotechnology. Other good practices in recycling of this kind of the waste can rarely be seen. However, one good example is the work of the “Magnetation” company in USA, which focuses toward the old iron mining hotspots, namely, abandoned waste stockpiles and tailings basins from the 18th century, and turns this waste into the usable technical iron [3]. They owe their success simply to the fact that magnetic separation of the small particles was not yet developed, while the 20th century technologies opened the door for this. However, this technology, although valuable also has its limits in the size of particles or the type of the iron ore (magnetic or not). Many mining hotspots full of other metals as well, need to be cleaned to expand the agricultural land, prevent the leaching of the metals to the soil and to the drinking water underground sources. Although these ecological emergencies are the priority without doubt, also, the economical part of such exploitation is not at all negligible. It would be excellent to be able to use 100% of the metal which was carried from deep underground with use of high amounts of energy and labor.
It is known even from the early human history that Bosnia and Herzegovina is a country which has a very dense distribution of the metal and coal mines comparing to the country surface area [4]. The most interesting hotspots for metal-based nanotechnology therefore might be as separated below.

Abandoned mines:

- “Smreka” Vareš Fe (hematite, siderite, limonite)
- “Veovača” Vareš Pb, Zn, Ba, Ag (HgS)
- “Olovo” Olovo, $PbCO_3$ (cerussite)
- “Čemernica” Fojnica, Sb, Ag (HgS)
- “Bakovići” Fojnica, Au, Ag (Fe)
- “Dubrave” Kreševo, Ba, Cu, Ag
- “Vihovići” Mostar, brown coal

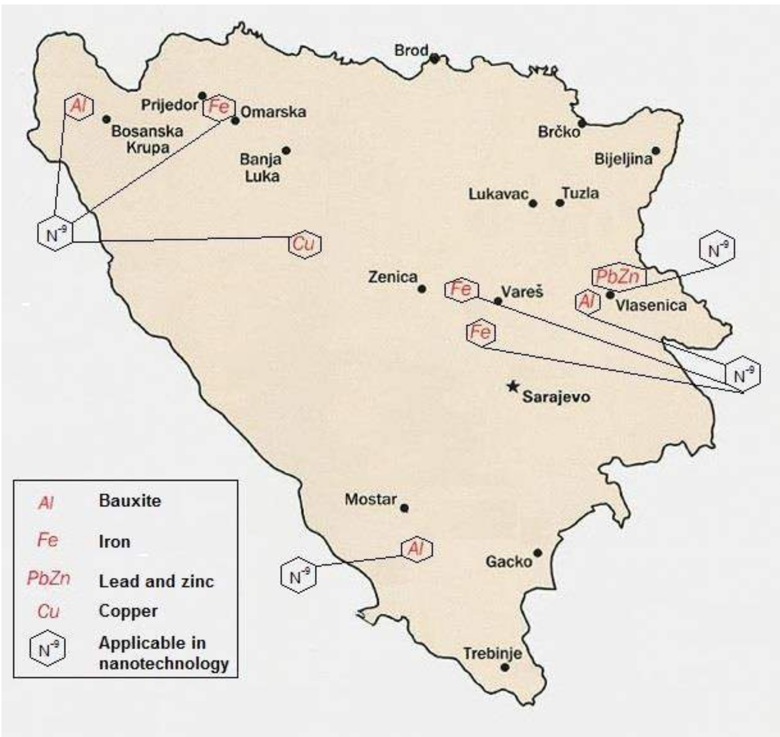
Metal mines still under exploitation with potential for nanotechnology (Picture 1.):

- “Milići”, Bauxite Al_2O_3
- “Posušje” Bauxite Al_2O_3
- “Čitluk” Bauxite Al_2O_3
- “Široki Brijeg” Bauxite Al_2O_3
- “Jajce” Bauxite Al_2O_3

- “Omarska” Ljubovija Fe
- “Sase” Srebrenica, Pb, Zn, Ag
- “Bosanska Krupa”, Bauxite Al_2O_3
- “Mačkare” Gornji Vakuf, Cu, Au

At each of these hotspots, often even the significant quantities of other trace metals can be found. They could also find their application some day in the future. For example, iron in Omarska mine is followed by significant quantities of manganese. Also, the presence of rare earth metals in traces cannot be excluded at these locations, since there is no systematic study about this subject.

At this point it is interesting to say few words about the deposits for which there was some research but the mine was never opened for exploitation. In particular, there are proven reserves for metals like Ni and Co at deposit „Tadići“ near Živinice. Nickel was also found in spring water “Ljubače” which is directly connected to the mentioned deposit. It was present in such quantities that the Beer factory in Tuzla gave up from using that water in production of beer. Strong pollutant present in Bakovići, an old gold and silver mine, is a halkopirite ($CuFeS_2$). This mineral, in reaction with water produces a sulphuric acid (H_2SO_4) which is of course very dangerous. “Veovača”, the Pb and Zn mine was also showing the presence and even produced some Ag ore. However, the problem was a high content of HgS. Despite being interesting for metal recycling, unfortunately, heavy metals in many open pit lakes have huge impact on people living there and the environment due to threat to water toxicity [5]. Therefore a sustainable solution for their removal and, if possible their putting into the market in some form, such as nanomaterials is highly desirable.



Picture 1. The map of currently functioning mining locations in Bosnia and Herzegovina, only for the metals applicable in nanotechnologies

2. PHYSICAL ASPECTS OF PROPERTIES CHANGE FROM BULK TO NANO-METALS

After stressing out the importance of the metal mining for human history, it is now important to stress out why the nano-dimensions of the metal are so attractive and why are they so different from the bulk metal.

At the present level of the nanomaterials development, metal nanomaterials are maybe not the most widely studied if analysed from the number of publications point of view. Their research has, nevertheless, resulted in the highest number of patents and they are the most commercialized group of nanomaterials.

Incredible changes in properties happen when the metal decreases from the bulk mass to the nano-level which is as close to atomic level as possible, practically from the macroscopic to nanoscopic scale. If we define work function as the amount of energy needed to remove an electron from the bulk solid, then in a cluster with less than 100 atoms – the amount of energy needed to ionize it (or to remove an electron from the cluster) differs from the work function. Clusters of gold have been found to have the same melting point of bulk gold only when they contain 1000 atoms or more. Melting point of the gold nanoparticles increases with gold-particle diameter [6]. For copper that number is 100 atoms or more. In general, "border" between nano-clusters and bulk depend on the property being measured.

Magnetism is the next important property of metals that should be addressed in aspect of bulk to nano transition. Most of the atoms in solids do not have a net magnetic moment, but some transition atom ions such as iron, manganese and cobalt (with partially filled inner d-orbital levels) posses a net magnetic moment. Within the cluster, the magnetic moment of each atom will interact with the moments of other atoms resulting in aligning of all the moments in one direction, with respect to the symmetry of the cluster. The result is that cluster will be magnetized and that could be measured (Stern-Gerlach experiment). For magnetic nanoparticles the measured magnetic moment is found to be less than the value for the perfect alignment of the moments in the cluster, caused by the vibrations of the atoms. The component of the magnetic moment of an individual cluster will interact with an applied DC magnetic field and align more likely parallel than antiparallel to the field. The overall net moment will be lower at high temperatures – it is inversely proportional to the temperature. That effect is known as superparamagnetism. One of the most interesting properties of nanoparticles is that even clusters made of nonmetallic atoms can have a net magnetic moment. One of the examples is rhenium which shows increase of its magnetic moment when cluster contains less than 20 atoms [7]. It is therefore significant to find additional sources of this rare earth metal, such as separation from the mining sludge which is discussed within this paper.

The bulk magnets vary from "soft magnetic materials" with small hysteresis area to "hard magnets" with large coercive fields and widest possible hysteresis loop. Nanostructuring of bulk magnetic materials can be used to design the magnetization curve. It is possible to even design nano-magnetic material with almost no hysteresis. These kinds of materials are superparamagnetic and are synthesized for nanosized powders of Ni-Fe-Co [8].

Today strongest permanent magnets are made of neodymium, iron and boron. The effect of the size of nanoparticle grain structure of $Nd_2Fe_{14}B$ shows that the coercive field decreases significantly below ~ 40nm and remnant magnetization increases [9]. Even more increase of remnant magnetization is to make nanoscale composition of hard $Nd_2Fe_{14}B$ in soft α-phase of iron (which is probably due to the exchange coupling between the hard and soft nanoparticles). For the hysteresis loop very important is the Ms (value of the saturation magnetization). The size of the magnetic nanoparticles has also been shown to influence the Ms in such a way that magnetization increases significantly below grain size of 20 nm.

This is very important result showing that decreasing the particle size of a granular magnetic material can improve the quality of permanent magnets 0.
Metallic nanoparticles (in particular iron-oxide based magnetic nanoparticles) have shown high biocompatibility and could be used in imaging, drug delivery and ultra-sensitive bioassays. These superparamagnetic nanoparticles have greater surface-to-volume ratios and smaller size than their larger ferromagnetic counterparts **Error! Reference source not found.**. With so much iron in the nature, obviously, a great potential of Bosnia and Herzegovina to develop the iron nanomaterial industry exists. Even more so if numerous accumulations around iron mines and abandoned hotspots are used as sources of iron which will be discussed bellow.
In the global nanomaterials market, the value for metal nanomaterials overall was around 7 billion $ in 2015 0, with the most commercialized metal nanomaterials: zinc oxide, titanium oxide and metalloid SiO_2. If discussing the potential for these materials in Bosnia and Herzegovina, it must be emphasized that Zn mining is present with large accumulation lake along the mine.
Zinc shows ability to absorb the microwaves, such as electromagnetic waves. ZnO can be practically used as an absorbing material throughout the electromagnetic spectrum. This makes zinc oxide nanoparticles useful within military and commercial applications as a high-performance invisible material for absorbing extremely high frequency millimetre wave, visible light and infrared light. Its usefulness also extends to radioactive shielding for mobile phones and other devices.
ZnO is known as a very important semiconductor with wide bandgap (3.37 eV) and large exciton binding energy of 60 meV at room temperature, which makes its nanoparticles excellent near UV, UV absorber and also near infrared rays. They are widely used for skin care products and hair care products for protection against the sun's rays thanks to this property. Because of all these physical characteristics, ZnO nanomaterial has been investigated extensively in wide technological applications from catalytic, electrical, optoelectronic and photochemistry fields to the room temperature blue-ultraviolet laser region 0.
In chemical sense, ZnO is a gas sensing materials, sensitive to many sorts of gases with satisfactory stability, while as a promising material for dye-sensitized solar cells, ZnO demonstrates improved performance. In the form of thin film, ZnO is used for flat display screen usage and it could be used as alternative to the TiO_2 nanostructured electrode in Grützel-type photocells. Moreover, ZnO is also used as a material for realizing efficient light-emitting diodes, UV light-emitting diodes and room temperature lasers 0. Also, ZnO can be made as transparent and highly conductive, or as piezoelectric component as well.
The sources of aluminium in Bosnia and Herzegovina are also very extensive and therefore important. Aluminium nanoparticles are highly effective catalysts. When they are added into solid rocket fuel, they help improve combustion speed and considerably increase combustion heat and combustion stability. The burning rate of solid propellant can be 5-20 times higher using aluminium nanopowders compared to powders with larger particle sizes 0. Adding about 5-10% of aluminium nanoparticles into normal aluminium powder improves the sintering processes of ceramics, with high heat-transfer performance, increased density, and enhanced the thermal conductivity of sinter. Aluminium nanoparticles have good sintering ability even under low temperatures due to the large surface and superficial atom ratio.

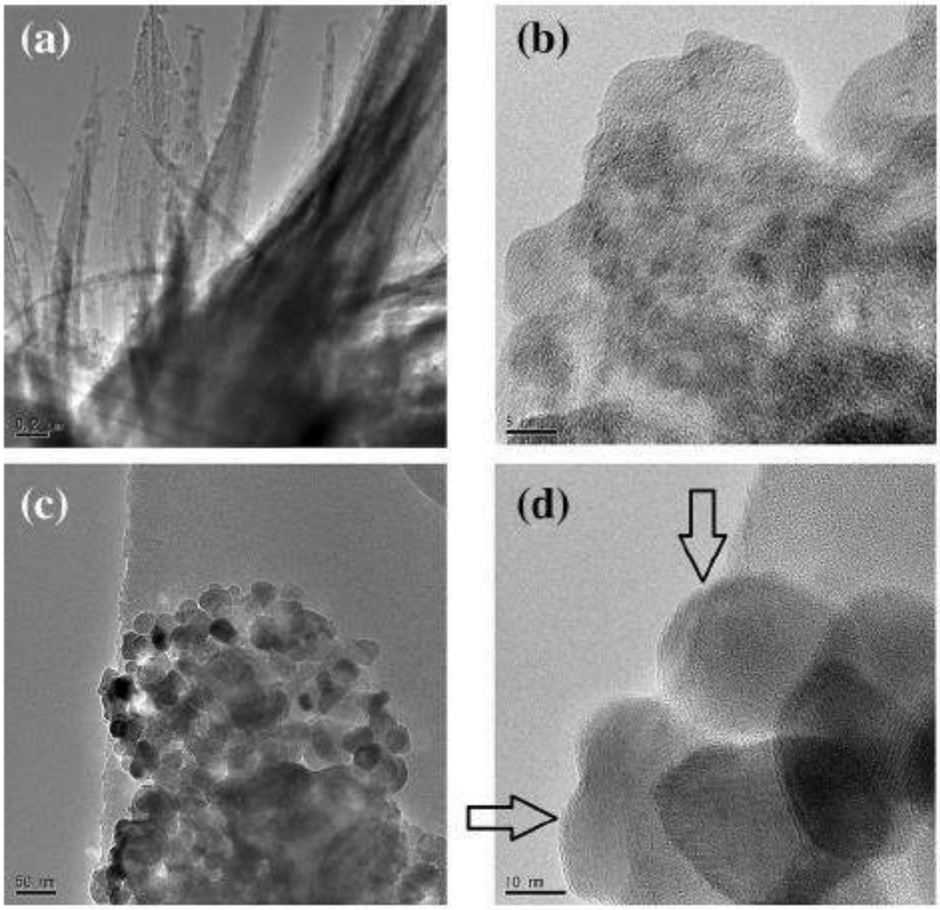
3. RESULTS IN NANOTECHNOLOGY BASED ON MINING WASTE IN BOSNIA AND HERZEGOVINA

Results from the University of Banja Luka research groups, show that metal mining hotspots carry a potential as the nanotechnology raw material resource [16, 17, 18]. These research activities are currently focused on Omarska iron mine in northwest of the country, where estimations go to more than 60 million tons of iron ore, mostly limonite which still can be recovered. However, according to the results, a lot of the fine, non-magnetic iron particles are dismissed and pass to the accumulation lake together with other components of the sludge in the ore-washing process. Stević et al. have found that there are beside iron, also quite significant quantities of the manganese contained 0. Taking into account that manganese is becoming scarce even cited as becoming one of rarer metals, than the value of such additional and available source of manganese is obvious. Not to mention if it this resource could be used for production of the manganese oxide nanoparticles useful in many applications 0.

They extract metals in various acidic digestion methods, than prepare the mixed ionic solution from extracted metals in water, and separate metals by means of classical analytic chemistry methods. Iron is extracted first with help of ammonium hydroxide and ammonium chloride.

The presentation of the results gained a lot of attention on recognised international conferences [16, 21] since no group in the world is currently dealing with the subject in the similar manner. The quality of their particles recently obtained was characterized and estimated at the collaborative laboratory in Nagano, Japan and have shown the market values of up to 1580 €/kg which shows directly the potential of the idea. Adding that metals are extracted by acid digestion with full possibility of the acid recycle, and resulting in non-toxic mostly silicate rubble obtained than the ecological side of the method is visible as well.

The particular particles recently published, represent a cheaply and easily obtained hematite core round-shaped metal nanoparticles (Picture 2.) with proven applicability in battery production. Namely, there are examples of the magnetite nanoparticles hybridized with the carbon for the battery application 0. Fe_3O_4 nanoparticles homogeneously embedded in two-dimensional (2D) porous graphitic carbon appear to be a durable high rate lithium-ion battery anode material with super high rate capability (858, 587, and 311 mAh/g at 5, 10, and 20 C, respectively, 1 C = 1 A/g) and extremely excellent cycling performance at high rates (only 3.47% capacity loss after 350 cycles at a high rate of 10 C). Other findings supporting this application are reduced graphene oxide/Fe_2O_3 composite used as an anode material for Li-ion batteries, their composite exhibited discharge and charge capacities of 1693 and 1227 mAh/g, respectively, with good cycling performance and rate capability 0.



Picture 2. Crystalline hematite nanoparticles with carbon shell with potential in environmentally-friendly battery production (cited with permission from 0)

Beside applications in batteries, iron oxide nanoparticles find their place in many areas of science and technology mostly in magnetic recording media [24, 25]. Also they are very valuable catalysts for CVD (chemical vapour deposition) synthesis of multi-walled carbon nanotubes 0 and in remediation of contaminants from waste water [27, 28]. A cost effective, reliable technology could be based on iron due to its dehalogenation efficiency, and benign environmental impact 0.
In summary, using iron or iron oxide nanoparticles instead of the traditional, more toxic, battery or catalytic materials is an exciting opportunity in which Bosnia and Herzegovina with its natural and human potentials could play an important role.

4. CONCLUSION

The potential of the metal mining waste hotspots was discussed in the frame of possibilities for production of the nanomaterials. This novel concept should be farther explored through the international collaboration between the countries which have the closed mines and abandoned hotspots, and countries like China, Brazil, India, and why not, also Bosnia and Herzegovina in which mines still perform intensive digging activities.
Acid digestion procedures are a cheap and powerful tool for extracting the waste metal ions from fine sludge which helps also to render the remaining rubble much less toxic. Obtained ionic solutions have the potential as the raw material for nanotechnologies while at the same time opens the possibility to find even some rare earth metals at unexpected places.

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