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# NON-FERROUS METALS-2011

Edited by  
Gennady L. Pashkov  
Peter V. Polyakov

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## IRON-BASED ULTRAFINE PARTICLES MADE IN MODEL SOLUTIONS AND INDUSTRIAL WASTE WATERS

M.I. Teremova<sup>1</sup>, E.A. Petrakovskaya<sup>2</sup>, A.S. Romanchenko<sup>3</sup>, F.V. Tuzikov<sup>4</sup>,  
Yu.L. Gurevich<sup>1</sup>, O.V. Tsibina<sup>1,5</sup>, E.K. Yakubailik<sup>2</sup>, Abhilash<sup>6</sup>

<sup>1</sup>Krasnoyarsk Research Center, Siberian Branch of RAS, Krasnoyarsk, Russia

<sup>2</sup>Institute of Physics, Siberian Branch of RAS, Krasnoyarsk, Russia

<sup>3</sup>Institute of Chemistry and Chemical Technology, Siberian Branch of RAS,  
Krasnoyarsk, Russia

<sup>4</sup>Institute of Catalysis, Siberian Branch of RAS, Novosibirsk, Russia

<sup>5</sup>Siberian Federal University, Krasnoyarsk, Russia

<sup>6</sup>National Metallurgical Laboratory (CSIR), Jamshedpur, India

Iron and attendant impurities settled from industrial waste water by ferritizing and formation of nanoparticles in batch bacterial culture have been studied. Iron settlement by ferritizing forms magnetic sediment extractable by magnetic separation. Settlement of iron and attendant impurities from model solution the bacterial culture forms superparamagnetic iron hydroxides. Magnetic and disperse characteristics of the sediment have been defined.

### Objects and methods

Synthesis of disperse particles by ferritizing [2, 5] was analyzed on model waste waters containing iron and attendant manganese, zinc and cobalt and in industrial waste water of non-ferrous metal processing plant. Industrial waste water contained iron and, in the form of impurities – copper, nickel, chromium, lead, zinc and manganese.

Environment conditions in precipitation of metal ions were evaluated in experiments carried out in compliance with design matrix of complete factorial experiment CFE 2<sup>3</sup> and orthogonal central composition design (OCCD) [4]. Controlled variables were: temperature; concentration ratio of ferrous and ferric iron  $[Fe^{2+}]/[Fe^{3+}]$ . Total concentration of iron was 5 g/l in CFE and 1 g/l in OCCD experiment. Iron-attendant metals were set in the form of water-soluble salts. Ion concentrations in CFE were (mg/l): Zn – 35, Mn – 160, Ni – 380. In OCCD experiments attendant elements were set in lower concentration – 18, 80 and 190 mg/l, respectively. All multifactorial experiments performed in compliance with design matrices, were carried out in two versions: in the first the source of trivalent iron was chemical reactant of ferric iron sulphate, in the second – of ferric iron produced by bacterial oxidation of the ferrous form. Residual concentration of metal in water was taken as measured response.

Efficiency and reproducibility of extraction of iron and attendant metals in the form of magnetic precipitation by ferritizing were evaluated on real (industrial) waste water with fluctuating composition of wastes.

Multifactorial experiments showed precipitation of iron and other metals to depend heavily on unidentified factor of bacterial origin. Therefore, the next series of experiments was aimed to study iron nanocrystallites in bacterial cultures. Bacteria (*Pseudomonas moorei*, *Pseudomonas argentinensis*, *Delftia tsuruhatensis* and *Bacillus mucilaginosus*) were cultivated in batch culture on mineral medium with iron citrate as the only source of carbon and energy and precursor of precipitating iron. Processes were carried with stirring and aeration with air in temperature range 26–34°C and initial pH 6.0–6.3.

Residual concentrations of metals in water after precipitation and isolation of the formed solid phase were evaluated by atomic absorption spectrophotometer. Iron status was defined by the data of Mössbauer spectroscopy with source Co<sup>57</sup>(Cr). Morphological characteristics of nanoparticles were produced on small-angle X-ray diffractometer S3-MICRO (Hecus, Austria) and multi-mode scanning probe microscope Solver P47 (NT-MDT, Russia). Spectra of electronic paramagnetic status were produced with X-range spectrometer SE/X – 2544 with nitrogen attachment.

## Results and discussion

Formation of hydroxides and iron oxides with magnetic properties in aqueous media is well known [1, 3]. This phenomenon is used to purify industrial waste waters from heavy metal ions by, e. g., ferritizing (2, 5 and other). Ferritizing is carried out at pH of the medium 8–10 and temperature 60–80 °C. We should note that the process is highly sensitive to temperature, pH,  $Fe^{3+}/Fe^{2+}$  ratio and total iron concentration. An example of real variability of ferritizing process in industrial waste water treatment is presented in tables 1 and 2.

Table 1

### Metal content in initial waste water and after ferritizing

Element	Concentration of metals in initial waste water, mg/l						
	Fe	Cu	Zn	Pb	Mn	Cr 3+	Ni
Variation limits	3840 – 11665	0.5–3.6	37.2–227.2	20.4–777.7	17–36.9	0.9–6.3	21.9–253.2
	Residual concentrations of metals, mg/l						
Variation limits	n/d–1.1	n/d–0.19	0.03–3.1	n/d–0.3	0.03 –1.57	n/d–1.1	0.05 –3.4
Mean values with overshoot (N=10)	0.356	0.03	0.343	0.01	0.22	0.032	0.642

Note: n/d – not detected (below sensitivity of the method).

Precipitation was most complete with lead and copper (in 7 and 4 out of 10 experiments, respectively, residual concentration was below evaluation threshold). The solid phase produced (crystalline sediment) is magnetically susceptible (table 3) and can be extracted by magnetic separator.

Measurements specific magnetization of sediments produced in treatment of industrial waste water under production conditions are presented in table 2.

Table 2

### Specific magnetization of sediment

Sample N°	1	2	3	4	5	6	7	8	9
Specific magnetization, Gauss·cm <sup>3</sup> /g	36.82	36.20	36.20	33.00	26.26	24.66	19.52	15.97	4.30

Operational parameters of ferritizing were invariable in all experiments. However, the quality of water treatment and magnetic characteristics of the sediment were observed to vary considerably. The process seems to be very sensitive to the accuracy of maintaining operational parameters. Meanwhile, total content of iron and attendant metals in real (industrial) waste water varies. In some situations organic compounds found in the water can have considerable impact [2]. To evaluate admissible variability of temperature, pH, ratio of reduced and oxidized forms of iron and its total content factorial experiments were carried out.

Design matrix and results of factorial experiment on metal settlement from model waste water by ferritizing are presented in table 1.

Design of factorial experiments and methods of processing results have been described in literature. Therefore, here we present results of experiments carried out only. Quantitatively the effect of environment parameters is described by (calculated by data from table 1) regression equations of form

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3$$

where Y is the residual concentration of metal,  $b_0$ ,  $b_1$ ,  $b_2$ ,  $b_3$  are the regression coefficients.

For residual concentration of iron in the version of experiments  $Fe^{ch}$  equation has form (in coded variable values)

$$Y = 161.3 + 65 X_1 + 36.9 X_2 + 46.9 X_3$$

Iron precipitation in the center of design (116.2 – experiment 9, version  $Fe^{ch}$ ) was considerably below the calculated values ( $b_0 = 161.3$ ). This means that degree of purification and residual concentrations of metal ions in water considerably and non-linearly depend on precipitation conditions (temperature, pH and  $Fe^{2+}/Fe^{3+}$  ratio).

Table 3

CFE 2<sup>3</sup> design matrix and experimental results

Factor	T	pH	Fe <sup>2+</sup> /Fe <sup>3+</sup>	Results of experiments							
Denotation	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>								
Units of measurement	°C	pH	relative units	Residual concentration (mg/l) Initial concentrations: Zn = 35, Mn = 160, Ni = 380, Fe <sub>total</sub> = 5000							
Lower level (-)	60	8	0.50								
Medium level (0)	65	9	0.75								
Upper level (+)	70	10	1.00								
Factors	T	pH	Fe <sup>2+</sup> /Fe <sup>3+</sup>								
Experiments	Coded values			Zn <sup>ch</sup>	Zn <sup>b</sup>	Mn <sup>ch</sup>	Mn <sup>b</sup>	Co <sup>ch</sup>	Co <sup>b</sup>	Fe <sup>ch</sup>	Fe <sup>b</sup>
1	-	-	-	0.10	n/d	23.0	n/d	5.70	n/d	94.0	n/d
2	+	-	-	0.05	0.03	15.2	n/d	1.95	n/d	24.6	n/d
3	-	+	-	0.06	0.05	96.0	n/d	25.0	n/d	226	n/d
4	+	+	-	0.05	0.05	86.0	n/d	19.5	n/d	160	n/d
5	-	-	+	0.05	0.05	64.0	n/d	10.0	n/d	112	n.o
6	+	-	+	0.12	n/d	112	n/d	33.0	n/d	314	n/d
7	-	+	+	0.03	0.03	4.16	n/d	0.02	n/d	n/d	n/d
8	+	+	+	0.05	0.03	32.0	n/d	21.0	n/d	360	n/d
9	0	0	0	0.05	n/d	15.0	n/d	1.80	n/d	11.6	n/d

Note: indices «ch» and «b» denote experiment versions in which iron (III) was used in the form of chemical reactant of ferric iron sulfate and bacterially oxidized ferrous iron sulfate, respectively; n/d – not detected.

Another important conclusion is that minimum residual concentrations of metal ions (less than 0.1–0.2 mg/l) are attained in the case of iron sulfate oxidized by bacteria. This indicates higher efficiency of metal precipitation with ferric iron sulfate produced by oxidation of its divalent form by bacteria. This seems to be the effect of some factor of bacterial origin. From the data of table 3 identical conclusions can be made for zinc, manganese and cobalt.

To have a better idea about dependence of metal precipitation on operating parameters of the process an OCCD-design experiment was carried out. Figure 1 shows results of analysis in the form of response surface, made by iron and manganese precipitation data.

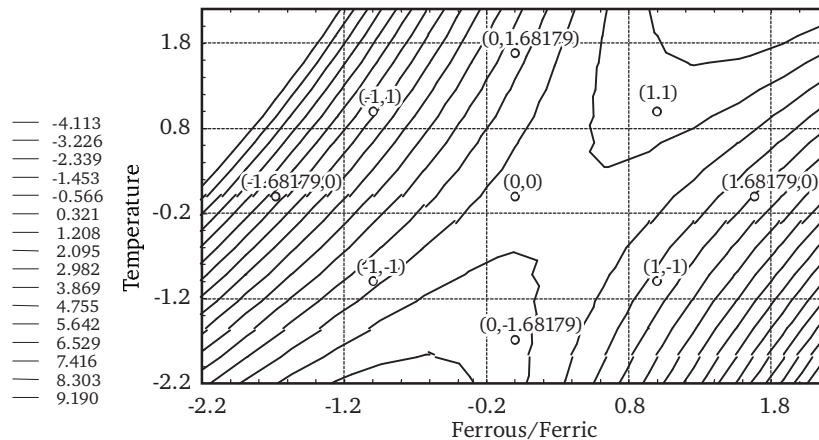


Fig. 1. Manganese precipitation vs. ferrous and ferric iron ratio

Figure 1 shows high and complex dependence of metal precipitation on environment parameters. In each specific case the maximum effect can be achieved only under strictly defined values of the said operating parameters. Moreover, bacteria used to produce ferric iron

had considerable effect. Judging by the microphotograph made with scanning-electron microscope the structure of precipitate in  $\text{Fe}^{\text{bio}}$  was polycrystalline. Individual particles of, probably, single crystal, sized had 4–10 nm. Metal ions obviously precipitated more efficiently in the presence of unidentified factor of bacterial origin. With this in mind special experiments were carried out to synthesize ultrafine iron particles in bacterial culture.

Different bacterial species were assumed to create essentially different conditions for precipitation of ions of iron and attendant metals. Originally we synthesized biogenic nanoparticles of iron hydroxide in microaerophilic culture of capsule bacteria *Klebsiella oxytoca* [6]. Bacteria *P. moorei*, *D. tsuruhatensis* used in this work have no capsule (extracellular matrix), bacteria *B. mucilaginosus* form extracellular substance of elevated viscosity, and in the culture of halotolerant bacteria *P. argentinensis* precipitation was running in the medium with high ionic strength of the solution (80 g/l NaCl).

By the data of Mössbauer spectroscopy all samples of bacterial nanoparticles are superparamagnetic iron hydroxides (mostly ferrihydrite). As opposed to ferrihydrite the nanocrystals of iron hydroxides formed in the microaerophilic culture of *K. oxytoca* bacteria, the nanocrystals of iron hydroxides from aerobic bacterial cultures are specified by small value of isomer shift (IS, nm/s in the range of 0.322–0.344) and presence of three nonequivalent sites of iron different in the quadrupole splitting (QS) value. In the sample from halotolerant bacteria *P. argentinensis* the isomer shift of the culture was higher (0.372–0.388).

Nanoparticles from aerobic bacterial cultures were analyzed by small-angle X-ray scattering (SAXS). Analysis showed their radius to be within 2–20 nm. Figure 2 shows size distribution of iron nanoparticles doped with zinc (solid line, *P. moorei*), cobalt (dashed line, *D. tsuruhatensis*) and nickel (dotted line, *P. moorei*). Distribution of nickel-doped nanoparticles somewhat shifted towards smaller size relative to two other samples which practically coincide.

At the same time atomic force microscopy identifies three image types – small, medium and large particles whose size is many times larger than SAXS-recorded particles with radius 2–4 nm. E. g., Figure 3 shows specific image of nanoparticles sizing about  $(60\text{--}90) \times (30\text{--}50)$  nm. Cobalt-doped iron hydroxide samples are observed to have small particles of elongated form with cross dimension  $(120\text{--}160) \times (50\text{--}70)$  nm and large spherical particles with diameter about 300 nm. The particles observed with AFM seem to be aggregates of single particles of nanosize.

Analysis of electron paramagnetic resonance spectra showed the material produced in cultures of aerobic bacteria to exhibit superparamagnetic properties. As the temperature drops, the resonance field decreases and the line broaden which corresponds to magnetic moment block, g-factor – 2.02 corresponds to iron particles. Material produced by nickel doping contains nickel clusters and iron-nickel particles with iron dominant. The amount of nickel in the latter is insignificant resulting in a small shift of the resonance field, but in considerable broadening of the line. Cobalt doping results in particles with pronounced magnetocrystalline anisotropy.

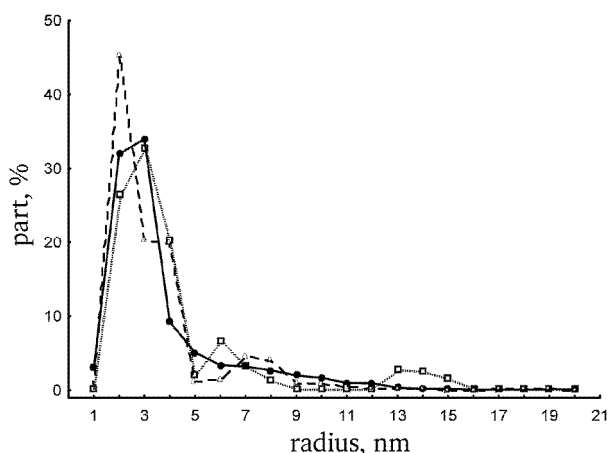


Fig. 2. Size distribution of nanoparticles (see explanation in the text)

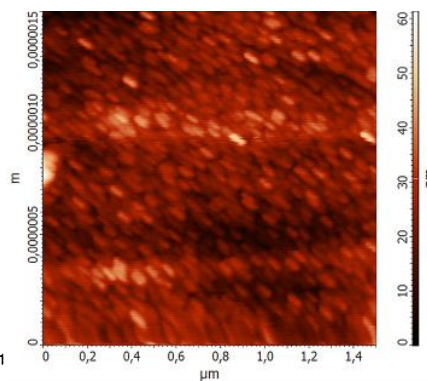


Fig. 3. AFM image of ultrafine iron particles deposited on pyrographite (tapping mode image)

On the whole by morphological characteristics and Mossbauer spectra obtained in aerobic bacterial cultures the iron-based nanoparticles are relatively uniform and the production process of nanoparticles is reproducible. Several experiments made possible to find that they exhibit catalytic and sorption properties and high biological activity. In this connection it is of interest to evaluate significance of observed differences.

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