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Composition and particle size of superparamagnetic corrosion products in tap water

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ABSTRACT

Chemical analyses, magnetization, Mössbauer spectrum, and x-ray diffraction measurements were made on solids removed from tap water by means of membrane filters. The taps from which this water was obtained had previously been unused for prolonged periods of time. When these taps were reactivated and water was first drawn, it was observed that the quantity of coarse solids in the water gradually decreased with flow, while at the same time the quantity of fine solids gradually increased. The magnetization, Mössbauer spectra, and x-ray diffraction patterns of the solids showed the presence of a significant number of superparamagnetic particles of magnetite. In the temperature range of our measurements ($77\ K < T < 300\ K$), paramagnetic iron-based species, particularly lepidocrocite, were also present in the solids. Contaminants such as Pb, Cu, and As were observed to be present in significant amounts, and it is shown that these are adsorbed to the magnetic nanoparticles. It was observed that almost all of the solid particles could be removed by means of 5-μm filters. This removal process can be explained by means of a model which assumes that initial deposition of coarse aggregates of corrosion products on the filters forms a coating, rich in extremely fine iron oxides. The coating has a high capacity for sorption of very small individual particles.

1. Introduction

Nano-size iron-bearing particles have been reported in tap water (Senftle et al., 2007). Colloidal dispersions of nanoparticles have particularly high surface activities (Moeser et al., 2002), and they can sorb contaminants, such as lead, arsenic, and copper (Nurmi et al., 2005). When the particles move through the pipe system, the sorbed contaminants are transported to the consumer. Accordingly, the chemical composition and size of particles in drinking water are important to the assessment of water quality. This is of particular importance because chemical analyses of water often focus on the concentrations of dissolved contaminants and ignore contaminants sorbed onto fine particles. The very fine particles may carry substantial amounts of contaminants.

In a previous paper (Senftle et al., 2007) it was shown that water samples of city water contained both multidomain ferromagnetic particles and aggregates of very fine (3.2–5.6 nm) superparamagnetic subdomain particles. However, the superparamagnetic magnetization was higher than the ferromagnetic magnetization. This fact clearly indicates the possible importance of subdomain particles as contamination

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carriers in tap water. It was also shown that a 0.22-μm membrane filter can be used to remove all of the particles from the water. Therefore it was decided to use a filtration technique supplemented by magnetic measurements to further study the particles. Chemical analyses have been made on the coarse and fine fractions of the solids separated by the filters as a function of collection time from several water taps, which were inactive for several months. Magnetic, Mössbauer spectral, and x-ray diffraction measurements were also made to help interpret the chemical and magnetic data.

2. Experimental Procedures

2.1. *Experiments using membrane filters*

Samples were obtained from several cold water taps in a 90-year old building in Washington, DC. Water is passed to the building by an underground cast iron pipe, but most of the water supply lines inside the building are made of copper alloy with soldered joints. The first sample from each tap was taken after the tap had not been in use for a period of at least several months. Additional samples were taken at weekly intervals. The tap was not turned on during the intervals between successive weekly samplings. Each sample (4 L) was filtered through a 5.0-μm membrane filter (Whatman Nucleopore 141113) to separate out the coarse suspended matter (>5.0 μm) and then through a 0.22-μm filter (Whatman Nucleopore 141128) to recover the fine solids (0.2–5.0 μm). The remaining solution constituted the filtrate. Fresh membrane filters (80% cellulose nitrate–20% cellulose acetate) were used for each filtration. The deposits on these filters were dissolved in a heated mixture of HCl and HNO_3, and then diluted with deionized water to a volume of 100 mL and analyzed using a Perkin Elmer Plasma 400 inductively coupled plasma (ICP) atomic emission spectrometer. The results were normalized to the original water volume by taking into account the 40:1 concentration increase upon deposition and dissolution. The filtrates which passed through the 0.22-μm filter were directly analyzed with the ICP spectrometer. Additional filtration experiments were performed using water from identical taps connected to the same water pipe in a single laboratory in order to acquire a sample large enough for the magnetic, Mössbauer spectroscopy, and x-ray diffraction measurements. Samples taken from the different taps on this same line were observed to have the same chemical composition and the same magnetic behavior.

3. Results of filtration experiments

3.1. *Composition of material trapped by filters*

A typical example of the composition of the filtrates and the particles on the filters from the first and seventh weekly samples of water from one of the taps is shown in Table 1. This table lists the concentrations of each element present in the water, including the concentration of that element present in the coarse suspended solids (>5 μm), in the fine suspended solids (0.2–5.0 μm), and finally in the dissolved and very fine solids (<0.22 μm) found in the filtrate. The concentration of all the elements is generally higher in the coarse material compared to the fine material reflecting the larger quantity of solids separated on the 5.0 μm filter. As expected, the much higher concentrations of some of the elements (e.g., Ca, Na, and Si) in the filtrate are due to the solubility of their compounds (e.g., $Ca(HCO_3)_2$, Na_2SiO_3) in water.

The changes in the total amounts of the elements as a function of the time of collection for the coarse fraction (>5.0 μm) of the solids, and for the fine fraction (0.22–5.0 μm) are shown in Fig. 1a,b, respectively. The results summarized in Table 1 indicate that the concentrations of the coarse solid particles decreased with time, while the concentrations of the fine solids showed an increase. In the samples of the coarse

Table 1 – Filtration of 4 L of tap water samples taken in the first and seventh weeks.

Element	Concentration (mg/L)					
	First sample			Seventh sample		
	>5.0 μm	0.22–5.0 μm	Filtrate (<0.22 μm)	>5.0 μm	0.22–5.0 μm	Filtrate (<0.22 μm)
Fe	3.47 ± 0.04	0.0019 ± 0.0001	0.004 ± 0.001	0.0070 ± 0.0001	0.020 ± 0.001	0.001 ± 0.001
Ca	1.77 ± 0.01	0.0008 ± 0.0001	32.9 ± 0.1	0.0063 ± 0.0001	0.011 ± 0.001	38.0 ± 0.5
Cu	1.59 ± 0.01	0.0003 ± 0.0001	0.051 ± 0.001	0.0042 ± 0.0001	0.012 ± 0.001	0.095 ± 0.007
Zn	1.27 ± 0.01	0.0004 ± 0.0001	0.13 ± 0.01	0.0084 ± 0.0001	0.013 ± 0.001	0.11 ± 0.01
Pb	1.14 ± 0.01	0.0004 ± 0.0002	0.014 ± 0.020	0.0052 ± 0.0003	0.0052 ± 0.0006	0.095 ± 0.005
Si	0.35 ± 0.01	0.0014 ± 0.0001	3.49 ± 0.03	0.0022 ± 0.0001	0.0021 ± 0.0001	2.97 ± 0.01
Mg	0.19 ± 0.01	0.0004 ± 0.0001	6.47 ± 0.02	0.0015 ± 0.0001	0.0019 ± 0.0001	9.89 ± 0.01
Al	0.19 ± 0.01	0.0002 ± 0.0001	0.14 ± 0.01	0.0015 ± 0.0004	0.0014 ± 0.0001	0.19 ± 0.01
Ni	0.12 ± 0.01	0.0001 ± 0.0001	0.032 ± 0.004	0.0020 ± 0.0001	0.0008 ± 0.0001	0.046 ± 0.001
Na	0.013 ± 0.001	0.0000 ± 0.0002	11.0 ± 0.1	0.0013 ± 0.0001	0.0004 ± 0.0001	15.7 ± 0.1
Ti	0.008 ± 0.001	0.0001 ± 0.0001	0.001 ± 0.001	0.0001 ± 0.0001	0.0001 ± 0.0001	0.002 ± 0.001
Mn	0.005 ± 0.001	0.0001 ± 0.0001	0.023 ± 0.001	0.0002 ± 0.0001	0.0002 ± 0.0001	0.003 ± 0.001
K	0.004 ± 0.001	0.0008 ± 0.0001	2.53 ± 0.03	0.0012 ± 0.0001	0.0012 ± 0.0003	3.07 ± 0.05
Mo	0.002 ± 0.001	0.0000 ± 0.0001	0.006 ± 0.001	0.0000 ± 0.0001	0.0000 ± 0.0006	0.000 ± 0.002
Cr	0.000 ± 0.001	0.0000 ± 0.0001	0.002 ± 0.001	0.0001 ± 0.0001	0.0002 ± 0.0001	0.000 ± 0.004
Total oxide	13.8 ± 0.1	0.010 ± 0.001		0.056 ± 0.001	0.096 ± 0.003	