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Superparamagnetic nanoparticles in tap water

Frank E. Senftle[a], *Arthur N. Thorpe*[a], *Julius R. Grant*[a,*], *Aaron Barkatt*[b]

[a]*Department of Physics and Astronomy, Howard University, Washington, DC 20059, USA*

[b]*Department of Chemistry, The Catholic University of America, Washington, DC 20064, USA*

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ABSTRACT

Magnetization measurements are a useful tool in the characterization of corrosion products formed in municipal water pipes made of iron or steel. Fine particles formed in corrosion processes exhibit superparamagnetic behavior. The size of such particles, which determines their capacity to adsorb hazardous species, can therefore be found from magnetic measurements. Application of this methodology to samples extracted from flowing and stagnant tap water, respectively, has shown that the flowing water samples contained multidomain (>100 nm) ferromagnetic particles as well as aggregates of very fine superparamagnetic subdomain particles. The sizes of the fine particles are of the order of 3.2–5.6 nm. In addition to small subdomain superparamagnetic particles stagnant water samples also contained larger subdomain particles with average dimensions of 59–67 nm. Both large and small subdomain particles were trapped by the fine charcoal in household filters.

1. Introduction

Municipal drinking water distribution systems throughout the world commonly use iron or steel pipes. Varma and Mathur (1990) have shown that as water flows from the water supply source through the carbon steel or iron pipes of the distribution system, it becomes enriched with respect to corrosion products. Particulate material of iron oxides formed on the pipe surfaces spalls off, and is carried away by the flowing water. These corrosion products range from coarse to very fine particles. As the adsorption of ions on insoluble particles is a significant function of particle size, it is important to investigate the very small particles present in water due to pipe corrosion. Nanosize particles of iron oxides and oxyhydroxides have a higher surface activity than coarse particles, and thus they adsorb significant amounts of hazardous species such as lead, arsenic, etc. (Nurmi et al., 2005; Yavuz et al., 2006). Therefore, such particles can become a potential health hazard. As nanoparticles take a long time to settle, they are likely to be carried by the water, along with the hazardous adsorbates, to the consumer. Several of the iron oxides (e.g. magnetite, maghemite, etc.) are magnetic and do form nanosize particles. It is the objective of this paper to use magnetic methods to detect and determine the size of magnetic nanoparticles in tap water.

1.1. *Particles of corrosion products in water pipes*

Corrosion scale studies by Feigenbaum et al. (1978) and also by Sarin et al. (2004) indicate that the scale can be divided into two distinct parts, i.e., a porous layer next to the inside surface of the pipe, and an outer dense shell of calcite and iron oxide compounds on the water side of the scale. Iron oxide compounds in the scales include Fe(III) phases such as lepidocrocite, goethite, and maghemite, as well as the mixed Fe(II, III) phase magnetite, while high concentrations of readily soluble Fe(II) compounds are present primarily inside the scales. In accordance with the findings of Feigenbaum et al. (1978), Benjamin et al. (1996), Sarin et al. (2001), Sarin and Snoeyink (2004), and Sarin et al. (2004), there is an increasing

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[*] *Corresponding author.* Tel.: +1 202 806 6255; fax: +1 202 806 5046.
E-mail address: jgrant@howard.edu (J.R. Grant).

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concentration of Fe_3O_4 toward the shell-like surface of the corrosion scale (the water side). Maghemite, lepidocrocite, and goethite are also reported by others to be present in this outer zone (Kölle and Rosch, 1980; Sontheimer et al., 1981). Corrosion reactions have been dealt with in great detail by Schwertmann and Cornell (1991), Cornell and Schwertmann (2003), Jones (1992), and Brubaker and Phipps (1979).

The exact morphology of scales in water pipes depends on factors such as concentrations of Ca^{2+} and O_2, time available for crystallization, etc. In particular, the cause of corrosion and the characteristics of corrosion products depend on the rate of water flow and replenishment (Cornell and Schwertmann, 2003). In practice, as water starts flowing through a pipe after a static interval, the conditions gradually change from stagnant to dynamic, resulting in changes in the corrosion processes and products. In general, any single water sample will not be exactly the same as the next sample from the same tap. However, by choosing suitable and representative samples, one can study the general magnetic properties of material extracted from drinking water from frequently used and seldom-used taps.

1.2. *Magnetic properties*

The solid products formed during pipe corrosion exhibit various types of magnetic behavior (Cornell and Schwertmann, 2003). Paramagnetic solids display a weak magnetization, which increases with magnetic field intensity due to partial alignment of uncoupled atomic moments, and also the saturation magnetization, M_s, is not attained except at extremely strong magnetic fields and low temperatures. Once the field is removed the alignment is relaxed, and the magnetization becomes zero. In contrast, ferromagnetic materials are characterized by an ordering of their atomic moments, even in the absence of an external field. These atomic moments are mutually coupled over relatively large regions of a magnetic particle called domains. Domain sizes generally range from 50 to 500 nm, and are typically around 100 nm (O'Handley, 2000). Bulk ferromagnetic materials are multidomain, and therefore the particle size exceeds the domain size by several orders of magnitude. Only relatively small magnetic fields are needed for the magnetization to reach saturation, i.e., to attain complete alignment of the magnetic domains with the field. After exposure to a magnetic field, some of the domains retain their alignment and the ferromagnetic sample has a permanent magnetic moment. In addition to the saturation value of the magnetization, M_s, two other parameters are needed to characterize ferromagnetic behavior. These are the remanent magnetization, M_r (i.e., the magnetization observed upon removal of the applied field), and the coercive force, H_c (i.e., the field that is needed to be applied in the opposite direction in order to reduce the magnetization from M_r to zero). Generally, the coercive force, H_c, for a given bulk ferromagnetic material is almost temperature independent. The dependence of the magnetization on the applied magnetic field for a bulk ferromagnetic material follows a hysteresis curve.

If the individual particles are subdomain in size, the observed magnetic behavior is no longer bulk ferromagnetic. Subdomain particles range in size from a single domain down to a few atoms. Above a certain temperature called the blocking temperature (T_B), except at very high fields, the magnetization of subdomain particles continues to rise with increasing applied magnetic field, and drops to zero, similar to paramagnetic behavior, once the external field is removed. Such magnetic behavior exhibited by subdomain particles of ferromagnetic material is called superparamagnetism. T_B tends to increase with particle size (Goya et al., 2003). Above the blocking temperature, the coercive force, H_c, is zero. At magnetic fields exceeding those that cause saturation of the magnetic particles, the total magnetization, M_T, of a mixture of multidomain, large subdomain, and small subdomain particles can be expressed by the Langevin function (Parekh et al., 2000) as

$$M_T = M_s + N_{sp}\mu\left[\frac{\cosh(\mu H/kT)}{\sinh(\mu H/kT)} - \frac{kT}{\mu H}\right], \tag{1}$$

where the bracketed term is the Langevin function, M_s is the saturation magnetization of the multidomain and large subdomain particles, H is the magnetic field, T is the absolute temperature, k is the Boltzmann constant, N_{sp} is the number of superparamagnetic particles, and μ is the magnetic moment of the superparamagnetic particles. We have used the above equation successfully in previous publications (Thorpe et al., 1990).

For the subdomain particles where $T<T_B$, total relaxation of the moments may not take place when the field is removed, and a hysteresis loop with a non-zero H_c is observed. The dependence of H_c on temperatures below T_B can be expressed by the following equation (Bean and Livingston, 1959):

$$H_c = \frac{2KV}{\mu}\left[1 - 5\left(\frac{kT}{KV}\right)^{1/2}\right], \tag{2}$$

where K is the anisotropic energy. For subdomain particles where $T>T_B$, H_c is zero, and thus, when mixed with ferromagnetic particles, H_c will be essentially temperature dependent.

To determine if nanoparticles are present in the water, it is necessary to determine the size of the magnetic particles. The approximate size for the magnetic particles with $T>T_B$ can be calculated if the high-field portion of the experimental hysteresis curve (M_T vs. H) is fitted to that given by Eq. (1), and the value of μ evaluated. The specific magnetization, σ, is defined as the magnetic moment μ of the superparamagnetic particle divided by its volume. Thus, the volume of the particle is $V=\mu/\sigma$. For bulk magnetite $\sigma = 450\times10^3\,\mathrm{A\,m^{-1}}$ in S.I. volume units. The volume and subsequent particle size so calculated must be considered approximate for the following three reasons: first, the value of σ is for bulk magnetite, second, a normal size distribution of the particles is assumed, and third, a spherical particle shape is assumed.

For particles with $T<T_B$, one can use Eq. (2) to determine T_B. T_B is the temperature where H_c equals zero. The slope, S, of the experimental plot of H_c vs. $T^{1/2}$ is $S=(-10/\mu)(kKV)^{1/2}$. The intercept of H_c at $T=0$ is $I=2KV/\mu$. After solving the previous two equations for μ by eliminating KV one obtains $\mu = 50kI/S^2$ (Thorpe et al., 2000). From the experimental plot of H_c vs. $T^{1/2}$, one can determine I and S and thus calculate μ, and the limiting size, $V=\mu/\sigma$, of the particles with this T_B (following the discussion of Candella and Haines, 1979). The diameter or