

Ekaterina Nikolskaya, Mika Liukkonen, Yrjö Hiltunen*

Real-time measurement system for determining metal concentrations in water-intensive processes

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***Corresponding Author: Yrjö Hiltunen:** University of Eastern Finland, P.O. Box 1627, FIN-70211 Kuopio, Finland, E-mail: yrjo.hiltunen@uef.fi

Ekaterina Nikolskaya, FiberLaboratory, South-Eastern Finland University of Applied Sciences, Savonlinna, Finland

Mika Liukkonen: University Of Eastern Finland, Kuopio, Finland

1 Background

Tightening requirements for the environmental quality of mining and process waters require more efficient purification methods. However, today's commercially available water quality measurements are not able to cope with certain significant contaminants like metal and sulfate concentrations in real time. In addition, presently used water quality monitoring systems require regular maintenance and calibration, which reduces their cost-efficiency.

High-resolution nuclear magnetic resonance (NMR) spectroscopy is one of the most informative analytical method in chemistry, but it is difficult to apply it to online process control in practice. Time domain nuclear magnetic resonance method (TD-NMR) is becoming highly attractive for industrial applications due to relatively low price, mobility, easy operating, and simple sample preparation procedure.

2 Aims

In this paper, the TD-NMR technology has been utilized for monitoring the concentrations of metal ions in water-based solutions. The main focus has been on paramagnetic ions such as Mn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Zn^{2+} and Ni^{2+} , which are the principal metal components in mining waters. Different concentrations of single metals and mixtures of them, and real mining water samples have been used in the tests.

3 Materials and methods

TD-NMR is sensitive to the presence of paramagnetic ions, which makes it a potentially applicable technology for measuring metal concentrations in mining waters.

The relaxivity of metal ion reflects how the relaxation rates of a solution change as a function of concentration [C]. Since a metal ion may affect the two relaxation rates (R_1 and R_2) individually, there are two corresponding relaxivities, denoted by r_1 and r_2 . By definition

$$R_1 = r_1 \cdot [C] + \text{constant1}, \text{ and}$$

$$R_2 = r_2 \cdot [C] + \text{constant2}$$

Since R_1 and R_2 are given in seconds⁻¹ and [C] is measured in milligrams per liter, r_1 and r_2 have the units of l/mg s. Relaxivity depends on the temperature, field strength, and the substance within which the metal ion is dissolved.

4 Results

4.1 Single metals

In this paper, we have focused on the relaxation rate R_2 , and the relaxivities r_2 for several metal ions are determined. The results are presented in Table 1. It can be summarized that the measurement of the concentrations of single metals is very accurate in laboratory conditions.

To simulate the effect of metal precipitation, some laboratory measurements were conducted. In these tests, the relaxation rates R_2 of Fe^{3+} were measured as a function of the pH. The pH of the solution was increased by adding some sodium hydroxide (NaOH). The initial concentration of ions was 40 mg/l at pH 1. The concentrations of Fe^{3+} were then calculated by using R_2 and r_2 values (See r_2 value in Table 1.). The calculated concentrations of Fe^{3+} as a function of pH are shown in Figure 1.

Table 1. Relaxivities r_2 for metal ions obtained in water solution by TD-NMR. Figures in parentheses show the errors of the relaxivities.

Metal ion	Relaxivity r_2 (l/mg s)
Mn ²⁺	0.81765(226)
Fe ³⁺	0.28799(365)
Fe ²⁺	0.01194(1)
Cu ²⁺ (CuSO ₄)	0.01493(10)
Cu ²⁺ (CuCl ₂)	0.01443(14)
Ni ²⁺	0.01239(9)
Zn ²⁺	0.00069(1)

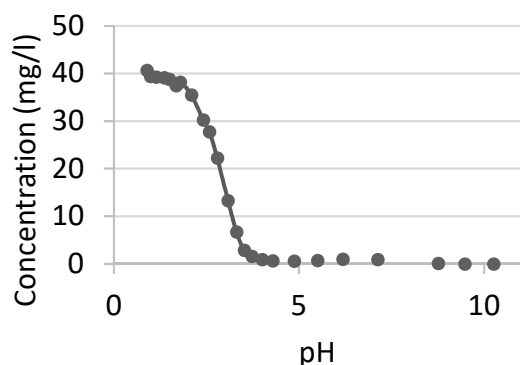


Figure 1: Fe³⁺ concentration as a function of the pH, calculated by R_2 measurements and the relaxivity presented in Table 1.

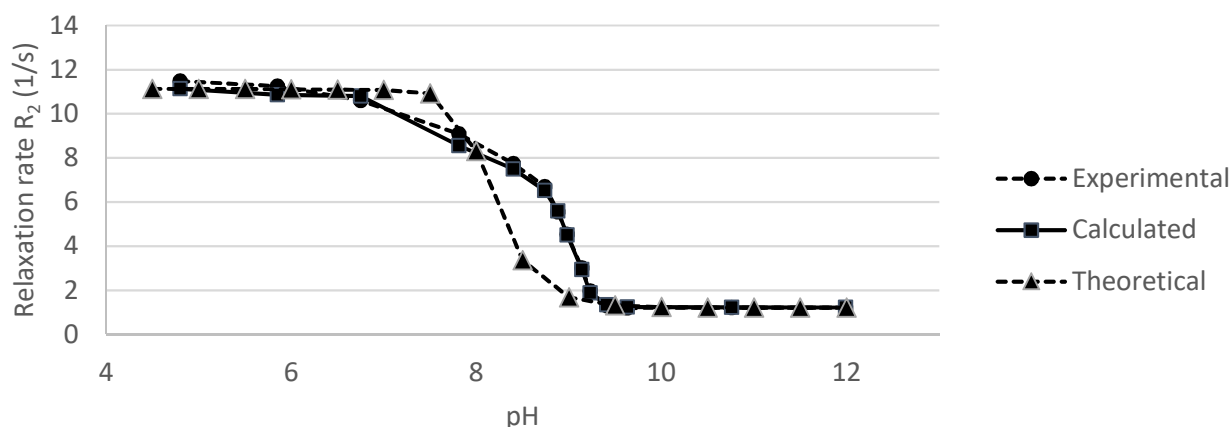


Figure 2: Independent components using the data contaminated by 0.5% of random failures.

4.2 Mixtures of metal ions

In real-world conditions, metals in waters typically exist in mixtures of several metal components. Therefore, a real mining water sample was also measured as a function of pH. These experimental relaxation rates of the water can be seen in Figure 2 (“Experimental”). The Mn, Fe, Cu and Zn concentrations of the samples were also measured by the x-ray fluorescence (XRF) method. Using these concentration values and the relaxivities presented in Table 1, the corresponding relaxation rates were calculated (Figure 2; “Calculated”). In addition, the concentrations of the metal ions were estimated by means of the ChemEQL software (<https://www.eawag.ch/en/department/surf/projects/chemeql/>), which is a computer program for calculating chemical speciation equilibria. Again, using these and r_2 values, the relaxation rates were calculated (Figure 2; “Theoretical”). As can be seen, all these different determinations are in a relatively good agreement with each other.

5 Conclusions

A real-time measurement system for determining metal concentrations in water-intensive processes was demonstrated in this study. The system includes a measurement device based on NMR technology, additional technology for transferring samples and controlling measurement conditions, the necessary software technology, protection housing, and cabling. These parts form the so called intelligent measurement system, which makes it possible to manage water processes and their metal concentrations better.