Research Article

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

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Abstract: The main purpose of this paper is to demonstrate the potential of time-domain nuclear magnetic resonance (TD-NMR) technology for monitoring the concentrations of metal ions in water-based solutions. The main focus of this work was paramagnetic ions, such as Mn$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Zn$^{2+}$, and Ni$^{2+}$, which are often the principal metal components in mining waters. Laboratory samples of different concentrations of single metals and mixtures of them and samples of real mining water were used in the relaxation rate ($R_2$) measurements. The measurements of single metal ions were used for the determination of the relaxivities of those ions. The concentrations of the ions in the mining water as a function of pH were also estimated by means of the X-ray fluorescence (XRF) method and ChemEQL software for calculating chemical speciation equilibria. Using these concentration values and the relaxivities of the metal ions, the total relaxation rate ($R_2$) results were then calculated. Principally, the results of these three different determinations are in relatively good agreement. It can be concluded that TD-NMR has great potential for monitoring metal ion concentrations during water treatment.

Keywords: NMR, time-domain, metal concentration, precipitation, mining water

1 Introduction

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 such as metal and sulfate in real time. In addition, the presently used water quality monitoring systems require regular maintenance and calibration, which reduces their cost efficiency.

Chemical precipitation is a conventional technology used to treat mining waters [1]. Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of precipitated solids from clean water. Typically, separation occurs in a clarifier, although separation by filtration or membranes is also possible. Chemical precipitation can also be applied in water pools, in which case the precipitated solids can simply be left at the bottom of the pool. Precipitation can be induced by the addition of an alkali, sulfide, coagulant, or other reagent that will bond with dissolved metal ions. Raising the pH with the use of alkaline reagents, such as sodium hydroxide, causes certain dissolved metals to precipitate as hydroxides.

Control of the effectiveness of heavy metal removal is essential in different applications [2–4]. It is important and necessary to use fast and accurate analytical methods that can be performed in real time. X-ray fluorescence (XRF) and atomic absorption spectrometry are typically used for heavy metal estimation. The nuclear magnetic resonance (NMR) technique could be an alternative to these methods. It was demonstrated that the limit of quantification of time-domain nuclear magnetic resonance (TD-NMR) is one order of magnitude larger than that of atomic absorption spectrometry; however, TD-NMR is a more robust and less expensive technique [5]. The main advantages of NMR are that it does not destroy the sample, it can be automated, and it is a non-fouling method.

High-resolution NMR has been extensively used in analytical chemistry, but in practice, it is difficult to apply to online process control due to its open magnetic field, large area of influence, high price and required cryogen use. On the other hand, the simpler TD-NMR method is becoming attractive for industrial applications due to its relatively low price, mobility, ease of operation, and simple sample preparation procedure [6–8].

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TD-NMR is broadly applicable in practical use, and it could potentially be utilized for intensive water process characterization, as NMR relaxation rates are sensitive to paramagnetic ions present in solutions. For example, NMR relaxation times were used to determine the concentrations of various paramagnetic ions (Co\(^{2+}\), Cr\(^{3+}\), Cu\(^{2+}\), Fe\(^{3+}\) and Mn\(^{2+}\)) \[9, 10\] and the solubility product of paramagnetic cations (Fe\(^{3+}\), Cu\(^{2+}\) and Mn\(^{2+}\)) \[11\] and to investigate the precipitation of mixtures of paramagnetic ions as a function of pH \[10, 11\]. Several investigations were performed by in situ TD-NMR \[9, 12\] by placing the sample on the NMR probe, and the NMR parameters were measured continuously during the reaction or process.

Despite the mentioned advantages and broad applicability, TD-NMR is still rarely applied online \[13\]. Monitoring of mining water during its processing was tested by online TD-NMR for the first time in a real mine \[14\]. TD-NMR was also recently applied to the online analysis of several liquid materials during different processes, such as fatty acid mixing \[15, 16\], starch gelatinization \[17\] and black liquor evaporation \[18\]. Moreover, there is a high demand on process analytical tools in various industrial areas nowadays, and novel sensors, developed on the basis of NMR technology, could be beneficial \[19–21\].

In this paper, TD-NMR technology has been utilized for monitoring the concentrations of paramagnetic metal ions, such as Mn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\) and Zn\(^{2+}\), in water-based solutions. Different concentrations of single metals and mixtures of them and real mining water samples were used in the tests. First, the relaxivities of separate metal ions were determined by NMR. Then, the concentrations of the single metals were estimated by NMR during the precipitation reactions. Furthermore, the approach was demonstrated in the laboratory during the precipitation reactions of multiple ions in a simple mixture of metals and in real mining water. Additionally, simulation of the metal concentrations during this process was performed using ChemEQL software for calculating chemical speciation equilibria. Monitoring of the Mn\(^{2+}\) concentration in the output mining water was also demonstrated.

## 2 Materials and methods

### 2.1 Metal ion samples

Measurements were performed using samples made in a laboratory and samples of real mining water. The laboratory samples for the relaxivity measurements of single metal ions were made by adding compounds, including appropriate metal ions to drinking water. First, the pH of the water samples was adjusted to pH 1. Then, the concentrations of metal ions were varied so that their relaxivities could be estimated by a linear function. The measurements were performed for the following ions: Mn\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\). In addition, the relaxivities of Cu\(^{2+}\) were determined using two different Cu compounds, namely, CuSO\(_4\) and CuCl\(_2\).

For the mining water, the concentrations of metal ions were studied as a function of pH, which was increased by adding sodium hydroxide (NaOH). In the experiment, the pH level was increased from pH 4.6 to pH 12. The metal concentrations of the samples (in mg/l) were measured by the XRF method. Because the XRF method has certain problems detecting light atoms (e.g., Mg and Al), the concentrations were determined for Mn, Fe, Cu and Zn. In addition, the effects of Mg and Al ions on our NMR measurements are very small compared to those of other metal ions, and their concentrations are constant as a function of pH, which also supports the decision to leave these ions out of the analysis. The pH values and the metal concentrations of the samples are given in Table 1 and Figure 1.

### 2.2 Metal ion concentrations

#### Table 1: Concentrations of metals (Mn, Fe, Cu and Zn) in mine water samples (in mg/l) measured by XRF.

| pH | Mn (mg/l) | Fe (mg/l) | Cu (mg/l) | Zn (mg/l) |
|----|-----------|-----------|-----------|-----------|
| 4.62 | 11.98     | 6.206     | 2.325     | 15.051    |
| 5.61 | 11.689    | 4.399     | 1.873     | 15.194    |
| 6.6  | 11.705    | 0.853     | 0.081     | 9.812     |
| 7.62 | 8.971     | 0         | 0.008     | 0.294     |
| 8.15 | 7.678     | 0         | 0.005     | 0.045     |
| 8.73 | 6.49      | 0         | 0.006     | 0.018     |
| 8.97 | 5.349     | 0.015     | 0.014     | 0.013     |
| 9.12 | 4.021     | 0         | 0.009     | 0.013     |
| 9.22 | 2.1       | 0         | 0.007     | 0.005     |
| 9.38 | 0.82      | 0         | 0.005     | 0.203     |
| 9.57 | 0.149     | 0.008     | 0.007     | 0.007     |
| 9.82 | 0.036     | 0.013     | 0.01     | 0.017     |
| 10   | 0.011     | 0.018     | 0.006     | 0.007     |
| 11.03| 0.01      | 0.011     | 0.005     | 0.01      |
Figure 1: Concentrations of metal ions (Mn$^{2+}$, Fe$^{3+}$, Cu$^{2+}$ and Zn$^{2+}$) in mine water samples as a function of pH (based on the data from Table 1).

2.2 TD-NMR

NMR is based on the absorption of energy by nuclei placed in a constant magnet field, which occurs under the resonance of the frequency of nuclei precession and the frequency of their excitation. In the NMR experiments, the registration of interactions of the magnetic moments of atomic nuclei with each other and their surroundings takes place. The main parameters measured by NMR are the spin-spin $R_2$ and spin-lattice $R_1$ relaxation rates, diffusion coefficients and signal magnitudes in the time domain and the Fourier spectra in the frequency domain. The measured parameters characterize the molecular properties and structure of the materials.

TD-NMR is sensitive to the presence of paramagnetic ions [22], which makes it a potentially applicable technology for measuring metal concentrations in water-intensive processes. In this study, the $^1$H resonance frequency of the system was 26 MHz, and the temperature of the magnet was 30$^\circ$C.

Transverse magnetization decays were measured by applying the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence [23, 24]. The echo time was 6 ms, and the number of 180$^\circ$ pulses in the sequence was 600. The relaxation delay was 6 s, and the number of scans was 4. The durations of the 90$^\circ$ and 180$^\circ$ RF pulses were 6.5 and 15 $\mu$s, respectively. The transverse magnetization decays of solutions with different Cu$^{2+}$ concentrations are shown in Figure 2.

The relaxivity of metal ions reflects how the relaxation rates of a solution change as a function of its concentration C. As described in Bloembergen-Purcell-Pound (BPP) theory [22], the effect of paramagnetic ions is strong because their magnetic moments are higher than those of protons [10, 11, 22]. 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:

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

$$R_2 = r_2 \cdot C + \text{constant2}.$$ (2)

Since $R_1$ and $R_2$ are given in $s^{-1}$ and C is measured in mg/l, $r_1$ and $r_2$ have units of l/mg s. constant1 and constant2 are the relaxation rates of clean water. The relaxivity depends on the temperature, field strength, and the substance in which the metal ion is dissolved.

Online measurements of metal ions were carried out using a TD-NMR system [25], which has been modified for flowing samples [15, 17, 18]. A MATLAB software script written by the authors was used for controlling the pump, conducting the TD-NMR measurements, fitting the magnetization decays and calculating the relaxation rates.

The measurement procedure was as follows (Figure 3):

1. An input or output sample of a water treatment process was delivered to a container, where it was continuously mixed.
2. The pH of the sample was measured.

Figure 2: Four transverse magnetization decays of samples with Cu$^{2+}$. 

$R_2 = r_2 \cdot C + \text{constant2}$. (2)
3. The sample was automatically pumped through the magnet system. The pump was stopped. The transverse magnetization decay was measured.
4. The decay was fitted, and the NMR parameter was solved.
5. A model was applied to determine metals present in the sample.
6. The $R_2$ and $r_2$ values were used for determination of the metal ion concentrations via Equation 2.
7. A new sample was pumped in.

Figure 3: Flow chart of the measurement procedure.

2.3 Calculation of chemical speciations

The concentrations of the metal ions as a function of pH were estimated by means of ChemEQL software [26], which is a computer program for calculating chemical speciation equilibria. The experimental concentrations of the metal ions at pH 4.62 (see Table 1) were used as the initial ion concentrations. Then, the concentration at each pH was estimated by the ChemEQL software; finally, the total relaxation rate $R_2$ results were calculated as a function of pH using the following equation:

$$R_2 = \sum_{i=1}^{n} r_{2i} C_i$$

where $n$ is the number of ions, the $r_{2i}$ values are from Table 2 and the concentration $C$ is calculated by the software.

3 Results

3.1 Relaxivities of metals

In this paper, we focus on the relaxation rate $R_2$ and relaxivity $r_2$ results for several metal ions. The relaxivity measurements were conducted for the following ions: Mn$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$. In addition, the Cu$^{2+}$ relaxivities were determined using two different chemicals. As an example, the correlation between the chemical concentration of Fe$^{3+}$ and its relaxation rate $R_2$ is presented in Figure 4, showing a very high correlation. The results of all the ions are collected in Table 2. In summary, the measurements for the concentrations of single metals are very accurate.

Figure 4: Relaxation rate $R_2$ as a function of Fe$^{3+}$ concentration.

Table 2: Relaxivity $r_2$ results for metal ions obtained from a water-based solution by TD-NMR. Numbers 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)               |

3.2 Relaxation rates of metal mixtures

The participation of simple mixtures of metal ions was studied by TD-NMR in the laboratory. The relaxation rates of two mixtures of Mn$^{2+}$ and Fe$^{3+}$ ions in different concent
trations \((\text{Fe}^{3+} 20 \text{ mg/l} + \text{Mn}^{2+} 13 \text{ mg/l} \text{ and } \text{Fe}^{3+} 40 \text{ mg/l} + \text{Mn}^{2+} 20 \text{ mg/l})\) as a function of pH are shown in Figure 5. Remarkably, the relaxation rates of these two mixtures behave quite differently at pH values of 4–10. This is probably due to a change in the redox value of the mixtures. In the case of the latter mixture \((\text{Fe}^{3+} 40 \text{ mg/l} + \text{Mn}^{2+} 20 \text{ mg/l})\), the redox potential eventually increases so much that the precipitation of \(\text{Mn}^{2+}\) begins at a lower pH. The main conclusion to be drawn here is that the behaviour of mixtures of metal ions is, in general, observable by the TD-NMR method, even if the behaviour is controlled by changes in the redox potential of the solution.

### 3.3 Mining water measurements

In real-world conditions, metals in water are typically bound within mixtures of several metal components. Therefore, the relaxation rates of a real mining water sample were also measured, and the results were plotted as a function of pH. The experimental relaxation rates of the water are shown in Figure 6. (“Experimental”). The Mn, Fe, Cu and Zn concentrations of the samples were also measured by the XRF method. Using the concentration values in Table 1 and the relaxivities presented in Table 2, the corresponding relaxation rates were calculated using Equation 3 (Figure 6; “Calculated”). The error between the experimental and calculated \(R_2\) values was 2.9\%, which indicates the good accuracy of the NMR method. It also confirms that the NMR effects of Al and Mg ions are small compared to those of other paramagnetic ions.

In addition, the concentrations of metal ions were estimated by means of ChemEQL software [26]. Again, using these \(r_2\) values and Equation 3, the theoretical relaxation rates were calculated (Figure 6; “Theoretical”). All three determinations are in relative good agreement. The results show that among the measured, calculated, and theoretical results, there is a more dramatic decrease in the relaxation rate at lower pH values for the NMR measurements, whereas the decrease in the relaxation rate of the theoretical calculations starts later. The results indicate that the difference between the experimental and theoretical values may arise from the redox reactions of the experimental samples.
3.4 Online measurements

The approach was tested in a real process: the estimation of metal ion contents in mining water during continuous purification. In the test shown in Figure 7, the change in pH of the output of this process ranges between 7 and 10. According to the data from Table 1, the concentration of only Mn\(^{2+}\) can be detected. All the other metals are minor concentrations at these pH levels, so they could be neglected. The Mn\(^{2+}\) concentration was calculated using Equation 2, and the relaxivity of Mn\(^{2+}\) is presented in Table 2. \(R_2 = 1.27\) s\(^{-1}\) at pH = 11.05 was used as constant2 in Equation 2.

4 Discussion

In this paper, TD-NMR technology was applied for monitoring the concentrations of Mn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\), Fe\(^{2+}\), Zn\(^{2+}\), and Ni\(^{2+}\) ions in water-based solutions. These paramagnetic ions are often the principal metal components in mining waters. XRF measurements and chemical speciation equilibria calculations were compared to the TD-NMR results. The results show the potential of TD-NMR for monitoring metal ion concentrations in process and mining water treatment.

Determination of the concentration of single paramagnetic ions in aqueous solution by TD-NMR relaxation is a robust approach, as previously demonstrated [9–11]. Moreover, TD-NMR was applied to the online monitoring of the precipitation of metals in real mines [14], and several investigations were performed in situ by measurements of samples placed in standard NMR tubes or by single-sided NMR [9, 12]. However, TD-NMR technology has rarely been applied to the online determination of chemical concentrations in industrial environments.

The measurement of metals in liquid is a new field of research and business because reliable online determination methods for different kinds of metal ions in process and mining waters do not exist. The results of this work and earlier papers [14, 16–18] indicate that the online TD-NMR method is not sensitive to fouling. Specifically, TD-NMR was successfully applied for the determination of the content of solids in black liquor at a pulp mill in a long-term test [18]. This property may provide a cost benefit due to lower maintenance costs. When considering the potential for producing commercial products, the results of this approach may offer a starting point for achieving cost savings by reducing both energy consumption and chemical consumption.

Online measurement of metal concentrations will be the first step towards more efficient and optimized control of water-intensive processes. Better measurement and control enable the optimization of processes, making it possible to achieve optimal purification, energy savings via the optimization of mixing processes, and chemical savings via the optimization of chemical dosage.

In the long term, better management of metals in liquid makes it possible to reduce the environmental impacts of water-intensive processes; thus, the well-being of the people, plants and other point sources of release in a mine’s sphere of influence may improve.

5 Conclusion

The measuring system presented in this paper is applicable for continuous real-time monitoring of the concentrations of a number of paramagnetic ions in water and controlling the water purification processes. TD-NMR is a non-fouling technique and might be beneficial for use in harsh industrial environments, such as mines, and municipal or industrial wastewater treatment processes. The performance of the system in various water-intensive processes will be further tested.

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