A non-fouling online method for monitoring precipitation of metal ions in mine waters

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Abstract: Heavy metal pollution has become a serious environmental problem today. Chemical precipitation is a basic technology used for mine water treatment. Raising the pH with the use of alkaline agents causes certain dissolved metals to precipitate as hydroxides. pH instruments are normally applied to controlling this process, although they cause continual problems with cleaning. In this paper, an alternative, non-fouling method for monitoring this process is presented.

Keywords: Mining water, precipitation, metal ions, NMR, Time domain.

1. INTRODUCTION

Heavy metal pollution has become a serious environmental problem today (Fu et. al., 2011). The treatment of metal ions is of special concern due to their recalcitrance and persistence in the environment. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. In recent years, various methods for heavy metal removal from wastewater have been extensively studied. Chemical precipitation is a conventional technology used to treat mine waters (Fu et .al., 2011). Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Chemical precipitation can also be used in water pools, in which case the precipitated solids can simply remain in 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 ion. Raising the pH with the use of alkaline agents, like sodium hydroxide, causes certain dissolved metals to precipitate as hydroxides. Online pH meters are normally used for controlling this process. However, these instruments cause continual problems with cleaning for operators.

Time domain nuclear magnetic resonance method (TD-NMR) is also becoming highly attractive for industrial applications due to relatively low price, mobility, easy operating, and simple sample preparation procedure. The most successful applications of TD-NMR confirmed by international standards are solid fat content determination in food and water (ISO 8292: 2008) and oil content in oilseeds (ISO 10565: 1998). They are based on the difference of NMR parameters of water and lipids and a low exchange degree between these two fractions. A possibility to use the same principle for analysis of lipid content in microalgae (Gao et.

al., 2008), for analysis of oil content of olive mill wastes and municipal wastewater sludge (Willson et. al., 2010) was demonstrated. The international standard for hydrogen content determination in aviation fuels (ASTM D7171 – 05: 2011) has been developed recently. Metal ions, particularly paramagnetic ions, can also change significantly relaxation times in water and biological samples (Yilmaz et. al., 1999; Grunin et. al., 2013), which can be applicable to controlling treatment of mine waters.

In this paper, a novel online method for monitoring precipitation of metals in mine waters is presented. The method is based on the time domain NMR.

2. MATERIALS AND METHODS

2.1 Chemical analysis

Laboratory tests were done using real mine water. pH was 4.6 before alkaline treatment. In the experiment pH level was increased from pH 4.6 to pH 12. The metal concentration of the samples (in mg/l) were measured by XRF method. Because the XRF method has problems with light atoms (e.g. Mg, Al), values were measured for Mn, Fe, Cu and Zn. The pH values and metal concentrations of the samples are given in Table 1 (in mg/l).

Table 1. Concentrations of metals (Mn, Fe, Cu and Zn) in test samples (in mg/l).

pH	Mn	Fe	Cu	Zn	Total
4.8	11.98	6.21	2.33	15.05	35.562
6.75	11.71	0.85	0.08	9.812	22.451
7.81	8.971	0	0.01	0.294	9.273
8.4	7.678	0	0.01	0.045	7.728
8.74	6.49	0	0.01	0.018	6.514
8.88	5.349	0.02	0.01	0.013	5.391
8.98	4.021	0	0.01	0.013	4.043
9.14	2.1	0	0.01	0.005	2.112
9.23	0.82	0	0.01	0.203	1.028
9.41	0.149	0.01	0.01	0.007	0.171
9.63	0.036	0.01	0.01	0.017	0.076
10.76	0.011	0.02	0.01	0.007	0.042
11.99	0.01	0.01	0.01	0.01	0.036

Mine water in a real process before alkaline treatment was pH 4.6. In the experiment pH level was increased to pH 11 and then decreased to pH 7. The concentrations of metals in two samples are given in Table 2.

Table 2. Concentrations of metals in real samples (in mg/l).

pH	Zn	Cu	Fe	Mn
7.50	7.64	0.35	<0.5	7.7
8.50	0.50	0.03	<0.5	5.4

2.2 NMR measurements

Relaxation times measurements were done using a mobile NMR device with a ^{1}H resonance frequency of 25.7 MHz (Resonance Systems Ltd). The device was modified for online measurements in industrial conditions (Figure 1). The permanent magnet of 0.6 T has dimension of 140x190x150 mm weighting 19 kg. The diameter of sensor hole was 10 mm. CPMG (Carr-Parcell-Meiboom-Gill) pulse sequence for spin-spin relaxation time T_2 measurements was used.

Fig. 1. The NMR device modified for online measurements in an industrial condition.

3. RESULTS AND DISCUSSION

The spin-spin relaxation times T_2 of mine water were measured using the same NMR device both in laboratory and in a real treatment process. The pH and T_2 data were collected by varying amount of sodium hydroxide.

The laboratory values of the relaxation time T_2 as a function of pH in mining water (circle) are shown in Fig. 2. For comparative purposes, the similar experiment by varying amount of NaOH chemical was repeated in drinking water. They are also in Fig. 2 (triangle). As we can see in the figure, the relaxation time measured in mine water approaches the value of clean water, when the metal ion removal increases.
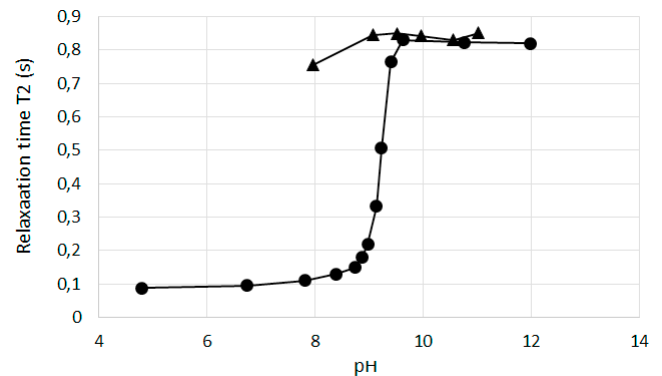

Fig. 2. Relaxation time T_2 of laboratory measurements as a function of pH in mine water (circle) and in drinking water (triangle).