SORPTION OF NICKEL ON MARL

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Batch sorption experiments using nickel have
been carried out on marl, a sedimentary,
carbonaceous rock. All experiments were per-
formed with a synthetic water of pH 7.3 and
in an atmosphere of N_2/1% CO_2. Over the
equilibrium nickel concentration range of
10^{-11}-10^{-5}M, sorption was linear and revers-
ible with R_d of 819 ml g^{-1}. Owing to the
linear sorption behavior, R_d was independent
of rock/water ratio (r/w = 1/5 - 1/100). The
data suggested that at [Ni] lower than 10^{-7}M
an isotope exchange mechanism operated,
whereas at higher [Ni], sorption involved
ion exchange. Sorption experiments on some
of the components of marl indicated that
nickel adsorbs mainly on the clay minerals
and on the trace of iron hydroxide present;
sorption on calcite and quartz was low.

INTRODUCTION

Interaction of nickel with rocks and soils is impor-
tant both because nickel is a heavy metal pollutant and
because the nuclides ^{59}Ni and ^{63}Ni may be released from

nuclear waste repositories[1-4]. The mobility of nickel
in the environment may be reduced by adsorption on rocks
and minerals. This is particularly relevant for waste
repository safety analysis, where an essential charac-
teristic of the host rock must be its ability to retard
radionuclide migration.

In Switzerland, one particular rock under considera-
tion as a host for a nuclear waste repository is marl,
a sedimentary, carbonaceous rock. The present report
describes the interaction of nickel with marl. The
studies described here, had the specific aim of deter-
mining the extent and kinetics of sorption of nickel by
marl. In addition, measurements were made to provide an
estimate of which components of marl sorbed nickel most
strongly.

MATERIALS AND METHODS

Marl was collected from the vicinity of Wellenberg
is central Switzerland. The sample consisted of 42%
calcite, 18% quartz, 22% illite and illite/smectite
mixed layer (illite:smectite = 2.5:1), 7% chlorite, 5%
ankerite, 3% kaolinite, 0.3% pyrite, 0.6% iron(III)
hydroxide and 0.5% organics. The BET surface area was
9 m^2. The cation exchange capacity was found by the
nickel ethylenediamine method[5] and was 9.0 meq/100 g.
For the sorption experiments, the marl was crushed and
ground using a tungsten carbide coated jaw crusher and
grinder, respectively. A sample with a particle size
<63 μm was obtained by dry sieving.

A synthetic ground water of composition 7.9×10^{-2} M Na^+,
1.2×10^{-3} M K^+, 2.7×10^{-3} M Mg^{2+}, 3.3×10^{-3} M Ca^{2+},
4.4×10^{-4} M Sr^{2+}, 2.6×10^{-4} M Si^{4+}, 1.4×10^{-4} M F^-,

8.1×10^{-2}M Cl^-, 4.5×10^{-3}M SO_4^{2-}, 4.4×10^{-3}M alkalinity and pH 7.3, was used for the sorption experiments. This composition is considered to be typical of that _in situ_. Before carrying out the sorption experiments, the marl and the marl water were equilibrated until a constant water composition was reached. This was done by holding marl suspensions in dialysis tubing (bags) in containers of synthetic water and renewing the water on a daily basis until chemical analysis showed no further change in composition (7 renewals). This equilibrated water and marl were then used for the adsorption/desorption experiments. Major ions were determined by inductively coupled plasma spectrometry (ICP), trace cations by inductively coupled plasma mass spectrometry (ICP-MS), anions by ion chromatography and alkalinity by acid titration.

The concentration of natural, stable nickel in synthetic marl water was 3.4×10^{-8}M and in equilibrated marl water, this concentration rose to 10^{-7}M, indicating some leaching of nickel from marl during the equilibration step.

Nickel solutions were prepared with ^{63}Ni tracer and inactive $Ni(NO_3)_2 \cdot 6H_2O$ in equilibrated marl water. The initial nickel concentrations ranged from 5.7×10^{-9}M to 10^{-3}M. All the solutions were stable (i.e. no detectable colloid or precipitate formation) over at least 7 weeks. ^{63}Ni was measured using liquid scintillation counting.

The speciation of nickel in synthetic marl water was calculated using the geochemical code Phreeque[6] and the following stability constants[1,7], lg $K(Ni(OH)_2) = 9.0$, lg $K(Ni(OH)_3^-) = 12.0$, lg $K(NiCO_3) = 6.87$, lg $K(Ni(CO_3)_2^{2-}) = 10.1$, lg $K(NiHCO_3^+) = 2.14$ and

lg $K(NiOH^+)$ = 4.14. These calculations indicated that
in synthetic marl water, the predominant nickel species
over the pH range of 7-9, is $NiCO_3$. At the pH of the
synthetic water (7.3), nickel was present as 89% $NiCO_3$
and 11% Ni^{2+}.

All adsorption/desorption experiments were carried
out in duplicate and with continuous agitation in an
atmosphere of N_2/1% CO_2 (appropriate to in situ condi-
tions) in a glove box. A complete series of experiments
with a rock/water ratio of 1/10 was carried out with
initial [Ni] from 5.7×10^{-9}-10^{-3}M. The effect of rock/
water ratio (1/5, 1/50, 1/100) was checked with
[Ni] = 1.1×10^{-7}M. The marl suspensions were held in dia-
lysis bags (to facilitate phase separation) suspended
in polyethylene flasks of spiked, equilibrated water.
Blanks (without marl) indicated that uptake of nickel
on the walls of the vessel at pH 7.3 was 3% and more
than 15% on the dialysis bags. Nickel uptake on the
vessel walls and dialysis bags in the presence of marl
was determined by acid leaching (M HCl) at the conclu-
sion of the experiments. In the presence of marl Ni up-
take on the vessel walls and the bags was no more than
2%; this was taken into consideration in the calcula-
tions of sorption coefficients (R_d).

The kinetics of sorption were followed using a bulk
suspension (20 g/200 ml) and a nickel concentration of
1.1×10^{-7}M. The suspension was sampled at intervals; the
total volume of all aliquots taken during the experi-
ments was less than 3% of the initial volume. Adsorp-
tion coefficients were calculated from the difference
between the count rates of the initial and final solu-
tion. Once the adsorption coefficients from the kinetic
experiments reached the steady state, all other suspen-
sions were sampled and measured.

TABLE 1

Sorption of nickel on some components of marl
(rock/water ratio = 1/10, initial [Ni] = 1.1×10^{-7}M,
pH = 7.3)

Components	BET surface area, $m^2\ g^{-1}$	R_d, ml g^{-1}
Calcite (Merck)	<1	5.7
Quartz (Merck)	<1	1.6
Goethite (FeOOH) (Bayer)	70	560
Kaolinite (Ward Ltd)	19.5	1913
Montmorillonite (Wyomming)	31.5	1109
Illite (Le Puy en Velay, France)	130	226

For the desorption step, the original solution was
replaced by tracer free, equilibrated, synthetic marl
water. The kinetics of desorption from the bulk sample
were followed until a steady state was reached after
which all other samples were measured.

The uptake of nickel on the components of marl was
carried out with pure materials, not with extracted com-
ponents because earlier work had indicated that extrac-
tion techniques could alter the properties (especially
the surface area) of the solids. The minerals used and
their sources are listed in Table 1. The samples were
equilibrated with synthetic marl water until the water
composition was invariant (24-48 h) and the solutions
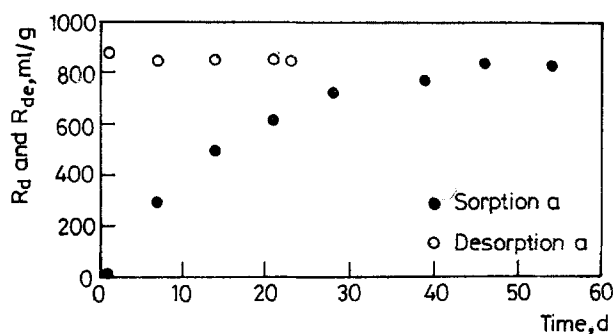then spiked with [63]Ni. The suspensions (r/w = 1/10,

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Fig. 1. Kinetics of sorption/desorption of nickel on marl expressed as sorption(R_d) and desorption(R_{de}) coefficients versus time
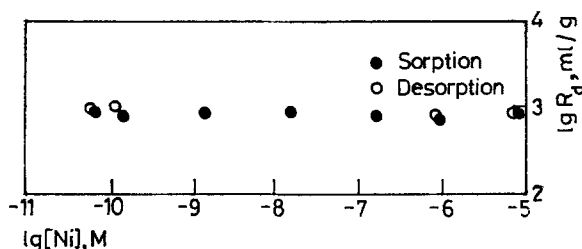

Fig. 2. Change in R_d and R_{de} of nickel on marl with equilibrium nickel concentration in solution

[Ni] = 1.1×10^{-7}M) were shaken in the glove box until equilibrium was reached (2 weeks), filtered (0.45 μm) and the activity of nickel in the filtrate measured.

RESULTS AND DISCUSSION

Figure 1 shows that the uptake of nickel by marl is slow; R_d reached a constant value only after 8 weeks. Desorption, however, was rapid and was complete in one week.

The changes in sorption/desorption coefficients as a function of equilibrium nickel consentration are shown in Figure 2. Adsorption is reversible and linear (i.e.

concentration independent) over the equilibrium nickel concentration range considered (10^{-11}- 10^{-5}M) with an R_d = 819 ml g^{-1}. The data were fitted to the Freundlich equation; the Freundlich exponent, N, was close to one (0.988) which is consistent with linear adsorption.

The concentration of natural, stable nickel in the equilibrated, synthetic water is 10^{-7}M. It is expected that when the concentration of nickel tracer is below the total [Ni], an isotope exchange mechanism would operate.

The bulk of nickel in the system was adsorbed by the marl, i.e. both $NiCO_3$ and Ni^{2+} species appear to have been taken up. This assumption, however, would imply different sorption sites and two different sorption mechanisms; this is not in accord with the observed linear sorption and fast desorption kinetics.

An alternative possibility is that Ni^{2+} is the pre-dominant adsorbing species and the decrease in [Ni^{2+}] following sorption will shift the equilibrium,

$$NiCO_3 \rightleftharpoons Ni^{2+} + CO_3^{2-}$$
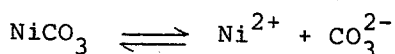
to the right, thus producing a further supply of Ni^{2+} for adsorption. The dissociation step may occur either in solution or, more probably, at the solid/liquid in-terface. This dissociation reaction may be rate-limiting and hence responsible for the slow adsorption kinetics. On the other hand, adsorbed Ni^{2+} could be readily re-moved by an ion exchange process and this could account for the fast desorption step.

Sorption of nickel on marl was independent of rock/water ratio (r/w = 1/5 to 1/100) over the entire [Ni] investigated. This is because, although the equilibrium [Ni] varied with the rock/water ratio, R_d remained in-variant as a result of the linear adsorption (Fig. 2).

This behavior of nickel contrasts with that observed for (non-linear) cesium sorption on marl, where R_d was strongly dependent on the rock/water ratio[8].

The data in Table 1 indicate that nickel adsorbs most extensively on the clay and iron hydroxide component of marl. As the iron hydroxide makes up only 0.6% of the marl, its contribution to nickel sorption can be expected to be low, unless this phase is present as a coating on the clay particles. The samples of calcite and quartz had far lower surface areas than the clays tested, which may partly account for the low sorption of nickel. However, preliminary tests on the extracted material suggested that in marl these components have a similar low surface area, hence, their contribution to nickel sorption is expected to be low.

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