1 **`Sequestration of metals in active cap materials: A laboratory and numerical**

2 **evaluation**

3

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8

9 **Abstract**

10 Active capping involves the use of capping materials that react with sediment contaminants to

11 reduce their toxicity or bioavailability. Although several amendments have been proposed for use

12 in active capping systems, little is known about their long-term ability to sequester metals.

13 Recent research has shown that the active amendment apatite has potential application for metals

14 contaminated sediments. The focus of this study was to evaluate the effectiveness of apatite in

15 the sequestration of metal contaminants through the use of short-term laboratory column studies

16 in conjunction with predictive, numerical modeling. A breakthrough column study was

17 conducted using North Carolina apatite as the active amendment. Under saturated conditions, a

18 spike solution containing elemental As, Cd, Co, Se, Pb, Zn, and a non-reactive tracer was injected

19 into the column. A sand column was tested under similar conditions as a control. Effluent water

20 samples were periodically collected from each column for chemical analysis. Relative to the non-

21 reactive tracer, the breakthrough of each metal was substantially delayed by the apatite.

22 Furthermore, breakthrough of each metal was substantially delayed by the apatite compared to the

23 sand column. Finally, a simple 1-D, numerical model was created to qualitatively predict the

1 long-term performance of apatite based on the findings from the column study. The results of the

2 modeling showed that apatite could delay the breakthrough of some metals for hundreds of years

3 under typical groundwater flow velocities.

4

5 **Introduction**

6 The extent of heavy metal contamination in soils and sediments is immense with important health

7 and economic implications (Knox et al., 2001). As such, there is an acute need for remedial

8 technologies that can address both a variety of contaminants in a range of aquatic environments

9 and provide permanent solutions by reducing contaminant toxicity. One of the conventional

10 remedies of contaminated sediments is passive capping which is the installation of a subaqueous

11 covering or cap of clean, inert material over contaminated sediment. Passive caps physically

12 isolate the sediment from the surrounding environment and reduce contaminant migration into the

13 overlying water. Conventional remedies have been proven to be effective for contaminants in

14 marine and freshwater environments; however, these technologies cannot be successfully applied

15 at all sites. Particularly problematic areas are those where dredging or passive capping are

16 impractical due to physical constraints, such as depth or presence of overlying physical structure

17 (e.g., docks, proximity to breakwaters).

18

19 In contrast to passive capping, active or reactive capping, which is targeted by the current study,

20 involves the use of capping materials that react with sediment contaminants to reduce their

21 toxicity or bioavailability. Active capping is a less mature technology that holds great potential

22 for a more permanent solution that avoids residual risks resulting from contaminant migration

23 through the cap or breaching of the cap and could be applied in areas where a more traditional

24 thick passive cap cannot be employed.

25

1 Although several active amendments have been proposed, only apatite has been evaluated for

2 active capping, but surprisingly little is known about the limitations of apatite (Knox et al., 2004,

3 Reible et al., 2006). Apatite is a phosphate-based material that has the potential to immobilize

4 lead and possibly other metals in contaminated soils/sediments (Knox et al., 2003, 2004, 2008

5 and 2010, Ma et al., 1995, Ma and Rao, 1997). Apatite is an economical, simple, and

6 environmentally friendly alternative to treat contaminated sediments compared to more traditional

7 treatment approaches. Other potential active amendments include organoclays, zeolite, activated

8 carbon, and possibly biopolymers, such as chitosan. Either individually or as mixtures, these

9 amendments have the potential to address both inorganic and organic contaminants in freshwater

10 and saltwater environments while limiting toxicity to existing flora and fauna.

11

12 The objective of this work was to evaluate the effectiveness of apatite in the sequestration of

13 various metals for potential use in active capping. Based on a simple, 1-dimensional numerical

14 model, the results of an apatite column study were used to predict the long-term effectiveness of

15 apatite in metals sequestration in comparison to nonreactive material, such as sand. Results from

16 the modeling exercise were also used to estimate the required cap thickness to delay contaminant

17 breakthrough for a specified period of time under typical field conditions.

18

1

2 **Methods and Materials**

3 *Measurement of Sorption Coefficients*

4 Sorption of As, Cd, Co, Se, Pb, and Zn in fresh water was evaluated for North Carolina apatite.

5 The experiment was conducted in 50 mL centrifuge tubes for one week. Each treatment had three

6 replicates: two for metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS)

7 and a third for pH measurements. The spike solution used in the experiment was obtained from

8 Inorganic Ventures, Lakewood, New Jersey. The metal concentration in the spike solution was 1

9 mg L^{-1} of As, Cd, Co, Se, Pb, and Zn. Suspensions composed of 0.2 g of solid (the sequestering

10 agent) and 15 mL of spike solution were shaken for one week, phase separated by centrifugation,

11 and then analyzed for metal content by ICP-MS and pH.

12

13 The metal concentration data obtained in this experiment were used to calculate partition

14 coefficient (Kd) values, defined as the ratio of the concentration of solute sorbed to the solid

15 divided by its concentration in solution. The K_d (mL g^{-1}) was calculated using Equation 1:

16

17
$$K_d = V_{spike} \left(\frac{C_{spike} - C_{final}}{C_{final}} \right) M_{mineral} \tag{1}$$
18

19 where C_{spike} is the metal concentration in spike solution before addition of amendment (mg L^{-1}),

20 C_{final} is the metal concentration in solution after contact with the amendment (mg L^{-1}), $M_{mineral}$ is

21 the amendment mass (g), and V_{spike} is the volume of spike solution (mL).

22

23 *Column Experiments*

24 Laboratory column experiments were conducted to evaluate the effectiveness of apatite in the

25 sorption and retention of various metals (As, Cd, Co, Se, Pb, and Zn). Two columns were tested

26 under saturated conditions, one packed with sand and one packed with apatite. The acrylic glass

Dixon   4

1 (Lucite) columns used in the experiments were 5 cm in diameter and 10 cm in length. Prior to the

2 start of the leaching experiments, the saturated hydraulic conductivity of both the sand and apatite

3 was estimated using a constant head method (Mariotte tube).

4

5 The sand column was initially leached with deionized (DI) water containing an ionic strength

6 adjuster (ISA) necessary for ion-selective analysis. The column was then leached with a spike

7 solution containing approximately 10 mg L^{-1} of each metal and 100 mg L^{-1} of bromide (NaBr).

8 The flow rate of the influent spike solution was maintained at 0.2 ml/min using a peristaltic pump

9 with flow upwards through the column. The effluent bromide concentration was continuously

10 monitored with an ion-selective electrode and recorded using a data logger. Samples of the

11 effluent from the column were collected for ICP-MS analysis using an auto-sampler (approximate

12 5 ml per sample).

13

14 Similar to the sand column, the apatite column was also leached with DI water containing an ISA

15 necessary for ion-selective analysis. The apatite column was then leached with a spike solution

16 containing 100 mg L^{-1} of bromide (NaBr). The flow rate of the influent spike solution was

17 maintained at 0.5 ml/min with flow upwards through the column. The effluent bromide

18 concentration was continuously monitored with an ion-selective electrode and recorded using a

19 data logger. Once breakthrough of the bromide tracer was achieved, the column was purged with

20 DI water to eliminate bromide from the column. Subsequently, the column was leached with a

21 spike solution containing approximately 2 mg L^{-1} of each metal. The flow rate of the influent

22 spike solution was maintained at 0.5 ml/min with flow upwards through the column. Samples of

23 the effluent from the column were collected for ICP-MS analysis using an auto-sampler

24 (approximately 5 ml per sample).

25

26

1   *Numerical Experiments*

2   A numerical analysis was conducted based on the results of the apatite column study to evaluate

3   the long-term effectiveness of apatite for the sequestration of metals contaminants. The purpose

4   of the analysis was not to exactly predict concentration as a function of time for each element.

5   Rather, it was intended to provide general insight into the behavior of the metals based on

6   measured and estimated material and transport properties for time periods much longer than were

7   tested under laboratory conditions.

8

9   Several input parameters to the numerical model were directly measured using standard methods

10   including dry bulk density, porosity, saturated hydraulic conductivity, and partition coefficient.

11   Breakthrough data for the column experiment were used to optimize the transport parameters

12   used in the model. This was accomplished using a parameter optimization method described by

13   Toride et al. (1999) and the computer code CXTFIT. An initial estimate of retardation factor and

14   dispersivity was obtained from CXTFIT using breakthrough data from the column experiment.

15   Subsequently, the simplified Ogata-Banks (1961) analytical solution to the 1-dimensional

16   advection-dispersion equation was used to further optimize the transport parameters to fit the

17   measured breakthrough data. The Ogata-Banks equation is given as

18

19
$$\frac{C}{C_o} = \left(\frac{1}{2}\right) erfc\left[\frac{\left(R_f x - v_w t\right)}{2\left(\alpha_x v_w t R_f\right)^{\frac{1}{2}}}\right] \tag{2}$$

20

21   where C is the time dependent concentration (mg L^{-1}), C$_o$ is the source concentration (mg L^{-1}), R$_f$

22   is the retardation factor (unitless), x is the position (cm), v$_w$ is the fluid velocity (cm/sec), t is time

23   (sec), and α_x is dispersivity (cm).

24

25   Once the necessary transport parameters were determined, a one-dimensional numerical model

26   was used to qualitatively assess transport of selected metals through the cap material as tested in

1   the laboratory column experiment. The generalized advection dispersion equation solved in the

2   numerical simulations is given in Equation 3:

3

4
$$R_f \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \qquad (3)$$

5

6   where R_f is the retardation factor (unitless), D is the dispersion coefficient (cm^2/sec), and v is the

7   fluid velocity (cm/sec). The retardation factor is defined in Equation 4:

8

9
$$R_f = \left(1 + \frac{\rho_b K_d}{n} \right) \qquad (4)$$

10

11   where ρb is the dry bulk density (g/cm3), K_d is the partition coefficient, and η is the porosity.

12   The dispersion coefficient is defined as in Equation 5:

13

14
$$D = \left(\alpha_x \, v \, t \right) \qquad (5)$$

15   The optimized dispersivity from Equation 2 was used to calculate the dispersion coefficient.

16   For the numerical analysis, a steady state advective flux of 0.001 cm sec^{-1} (equivalent to a column

17   flow rate of 0.5 ml min^{-1}) was applied to the model domain. Molecular diffusion was considered

18   negligible compared to mechanical dispersion. Simulations were conducted for a time period of

19   1,000 years.

20

21   **Results and Discussion**

22   Capping materials, used as barriers to prevent contaminant release, must maintain adsorptive

23   properties over fluctuating conditions of the aquatic environments, such as dissolved oxygen

24   concentrations, fluctuating temperatures, salinities, redox potential, and others. The results of the

25   sorption experiments were used to calculate the partition coefficient of each metal for North

1   Carolina apatite. These partition coefficients are presented in Exhibit 1. Apatite was shown to be

2   effective in sorbing each metal tested with Pb being the most strongly sorbed. Apatite binds

3   certain metals into insoluble phases that are extremely stable by replacing $Ca2+$, $PO43-$, and $OH-$

4   ions by metal ions and it can act as a geosorbent for other metals with binding strength affected

5   by solution pH (Chen et al., 1997, Kaplan and Knox 2004). Also, Crannell et al. (2004) showed

6   that apatite reduced Pb diffusivity by 67 percent and Zn by 50 percent. For example, Jho et al.

7   (2011) showed that Pb is more strongly bound on apatite than Cd. However, these kinetic studies

8   showed that, while the Cd desorption extent was enhanced by the presence of apatite, the rate

9   constant was not affected by the presence of stabilizing agents. Overall, this study suggests that

10   Cd stabilization with apatite is beneficial as the extent of the Cd desorption in sediment can be

11   enhanced (Jho et al., 2011).

12

13   *Advective Transport of Metals through Active Caps – Laboratory Evaluation*

14   The breakthrough curves for the sand column are shown in Exhibit 2. Based on the breakthrough

15   of the Br^- tracer, the porosity of the sand was estimated to be 0.4 with a pore volume of 84.6 ml.

16   The saturated hydraulic conductivity of the sand was estimated to be 5.23×10^{-3} cm sec^{-1}.

17

18   Approximately 3 to 4 pore volumes of solution were pumped through the sand column over a

19   period of about 24 hours and breakthrough of all metals was observed during this period. As

20   expected, breakthrough of the metals was similar in timing to breakthrough of the non-reactive

21   tracer. Exhibit 2 shows that the movement of the metals through the column was similar to the

22   non-adsorbed Br^- tracer. Initial breakthrough was almost identical for all species. However,

23   differences noticed at later time intervals may be attributed to analytical interferences associated

24   with the ICP-MS method.

25

1   A 1-dimensional numerical model based on Equation 3 was used to simulate breakthrough of the

2   Br⁻ tracer, Exhibit 2. Although not presented, material properties used in the model were typical

3   of a medium textured sand. Good agreement is noted between the predicted and observed tracer

4   breakthrough. This serves to show that the numerical scheme used was robust and accurately

5   represented the properties and flow conditions of the sand column.

6

7   Breakthrough curves for the apatite column are shown in Exhibit 3. Based on the breakthrough of

8   the bromide tracer, the porosity of the apatite was estimated to be 0.3 with a pore volume of 54.0

9   ml. The saturated hydraulic conductivity of the apatite was estimated to be 7.8×10^{-5} cm sec⁻¹.

10

11   Approximately 2,759 pore volumes of solution were pumped through the apatite column over a

12   period of about 207 days. Relative to the non-reactive tracer, the breakthrough of each metal was

13   significantly delayed by the apatite. Exhibit 3 shows that each metal was sorbed by the apatite

14   and delayed in breakthrough for several pore volumes. Further, the breakthrough of each metal

15   was significantly delayed compared to the Br⁻ tracer. Arsenic, cobalt, and selenium are the first

16   metals to appear in the column effluent. Compared to the other metals in the spike solution, these

17   metals should breakthrough the apatite column first based on the empirically determined

18   partitioning coefficients (Exhibit 1).

19

20   The 1-dimensional numerical model used to simulate contaminant movement in the sand column

21   was modified to simulate the apatite column. As previously described, an initial estimate of the

22   retardation factor and dispersivity was obtained with the cobalt breakthrough data using CXTFIT

23   (Toride, et al., 1999). Using the initial estimates obtained from CXTFIT, the transport parameters

24   were optimized using a visual curve matching technique and an analytical solution to the 1-

25   dimensional advection-dispersion equation (Ogata and Banks, 1961). For the analytical model,

26   both the retardation factor and the dispersivity were manipulated to fit the cobalt breakthrough

Dixon   9

1   data. The resulting dispersivity was estimated to be 3.48 cm, which is consistent with literature

2   values for saturated porous media (Giraldi et al., 2009). Using the analytical model, the

3   retardation factor was determined to be 476 which translates to a partition coefficient of 130 ml

4   g^{-1}. The estimated partition coefficient compares reasonably well to the measured value of 177

5   ml g^{-1}.

6   The breakthrough curves for cobalt predicted by the analytical and numerical models are

7   presented in Exhibit 4. The dispersivity obtained from the analytical model was used in the

8   numerical model whereas the laboratory measured partition coefficient was used to calculate the

9   retardation factor in the numerical model. The decision was made to use the laboratory measured

10   partition coefficient for cobalt since the simulations for the other metals also used laboratory

11   measured partition coefficients. Good agreement is noted between the solutions and both models

12   approximate the observed breakthrough data reasonably well.

13

14   The estimate for dispersivity obtained from the cobalt breakthrough data was used to model all

15   other contaminants for the apatite column. The simulated breakthrough curves for the metals of

16   interest are presented in Exhibit 5. These breakthrough curves are for the flow conditions tested

17   in the laboratory column study. The breakthrough of all the metals is significantly delayed

18   compared to the simulated tracer with lead being delayed the most. Our results are comparable to

19   those of Bostick et al. (2003) and Viana et al. (2008) where they found that apatite successfully

20   retarded migration of Pb, Cd, and Hg, but was less effective for As, Ba, and Cr.

21

22   The numerical model was also used to create nomographs that relate cap thickness to time for

23   various flow rates. These nomographs can be useful in cap design for estimating the required

24   thickness of amendment to delay contaminant breakthrough for a specified period of time.

25   Example nomographs are presented in Exhibits 7 and 8. These nomographs were created for

26   various column flow rates but could easily be converted to groundwater velocity simply by

Dixon   10

1   dividing the flow rate by the area of the column. Cap thickness is clearly the most important

2   factor especially under diffusion. Viana et al. (2008) showed that a sand cap performed best under

3   diffusion due to the greater diffusive path length. However, an inadequately armored sand cap

4   layer alone may not work satisfactorily, even in sites that are only under diffusive transport

5   conditions due to erosive losses of cap material over time.

6

1

Conclusions

3 Breakthrough column studies were conducted to evaluate the effectiveness of apatite in the

4 sequestration of various metals in comparison to a neutral material, sand. As expected, the

5 laboratory column study showed that breakthrough of the metals in the sand column was similar

6 in timing to breakthrough of the non-reactive tracer. Also, relative to the non-reactive tracer, the

7 breakthrough of each metal was significantly delayed by the apatite.

8

9 In addition to the laboratory column studies, a one-dimensional numerical model was used to

10 qualitatively assess the transport and retention of the metals through both the sand and apatite

11 columns. Good agreement was noted between the predicted and observed contaminant

12 breakthrough for the sand column.

13

14 For the apatite column, an analytical model was used to calibrate the transport parameters used in

15 the numerical model based on the cobalt breakthrough curve. The retardation factor was fixed

16 based on the laboratory measured partitioning coefficient and the dispersion coefficient was

17 varied to obtain the optimum fit. Once the optimum dispersion coefficient was determined using

18 the analytical model, it was fixed in the numerical model for all analytes. The numerical model

19 was then used to estimate the required amendment thickness to delay contaminant breakthrough

20 for a specified time period given specific field conditions.

21

22 Overall, results from this study show that reactive amendments, such as apatite, can significantly

23 delay the breakthrough of certain contaminants compared to sand. This illustrates the promise of

24 amendments such as apatite for use in active cap systems. In addition to the breakthrough

25 experiments conducted as part of this study, a simple numerical model was used to estimate the

26 required cap thickness to delay contaminant breakthrough for a specified time period for various

1   flow rates. The numerical model serves as a cost effective tool for use in the design of active cap

2   systems.

3

4   The study results demonstrate the need for uncertainty analysis, which is driven primarily by

5   sediment chemistry that greatly affects K_d and the variety of cap materials with different

6   permeabilities. More K_d data under realistic field conditions are needed to reduce uncertainty to a

7   level more acceptable in managing risk.

8

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18

1

2   Exhibit 1. Average K_d values (standard deviation) for nine elements for each tested amendment
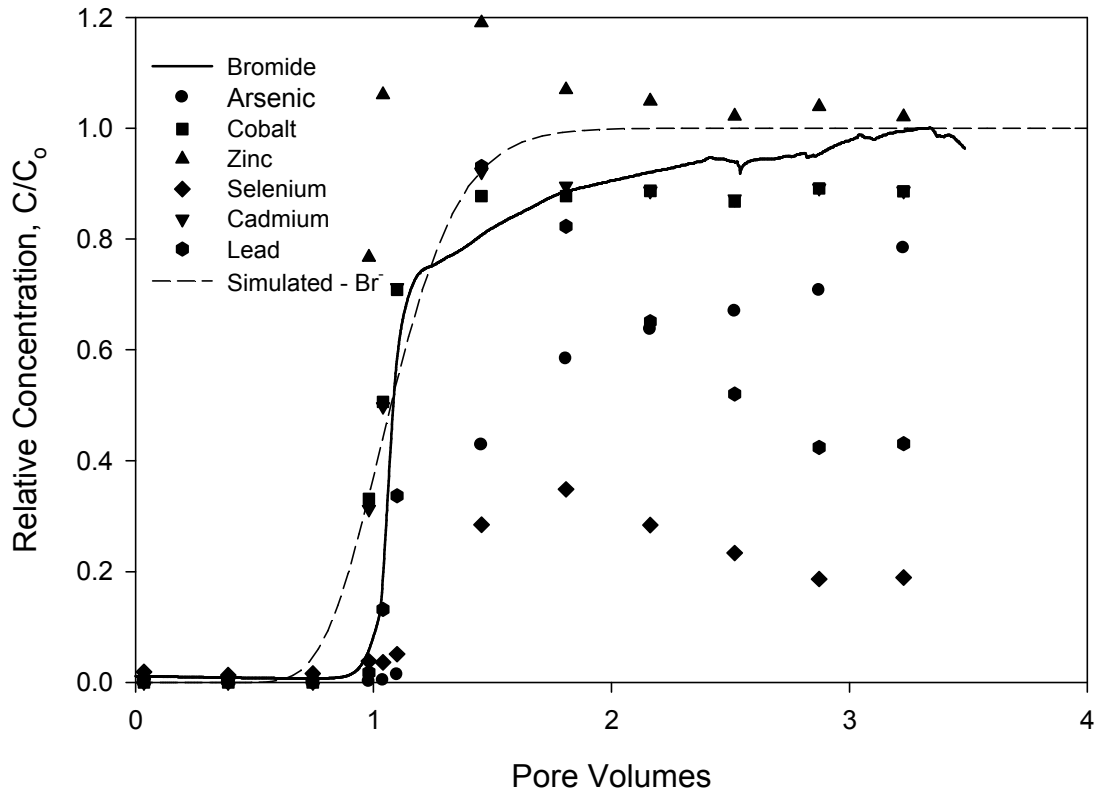
3   (in mL g^{-1}).

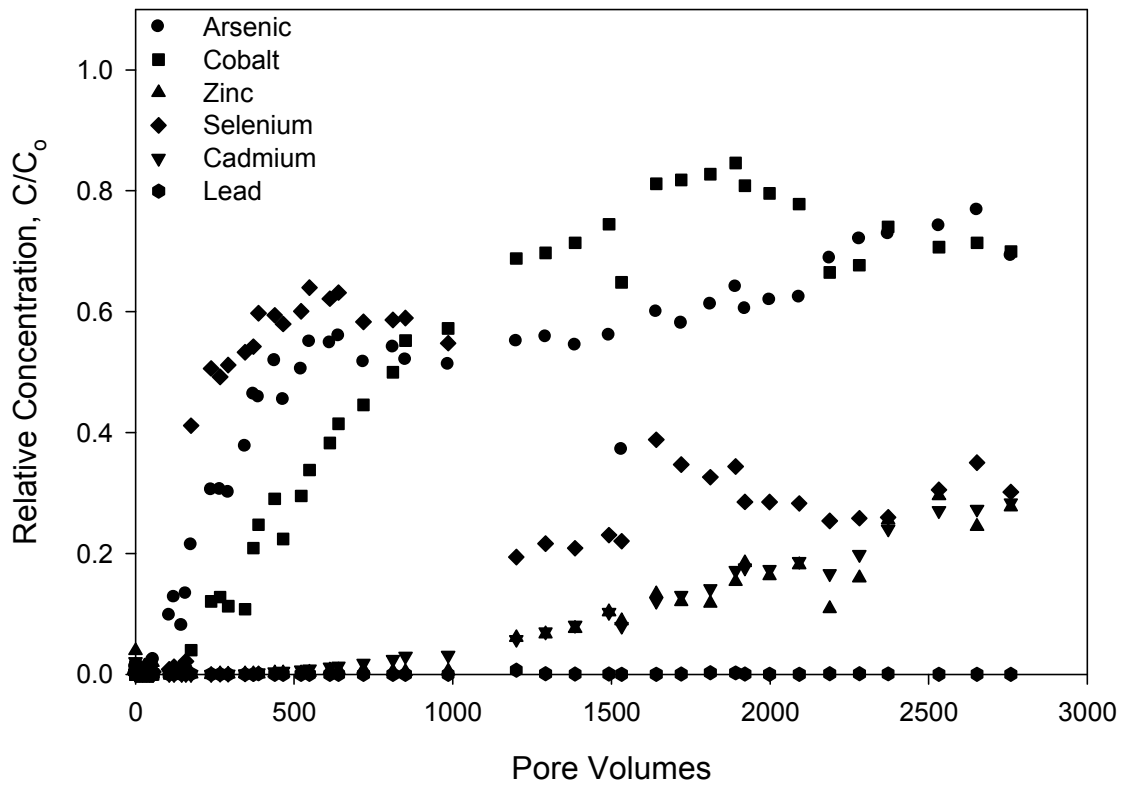| Element	Apatite[1] (NCA)
As	65.4
Co	176.6
Cd	4050
Pb	10940
Se	85.7
Zn	5009

4   [1]North Carolina Apatite
5

6

1

2

3   Exhibit 2. Breakthrough curves for the sand column including simulated non-reactive tracer.

4

1
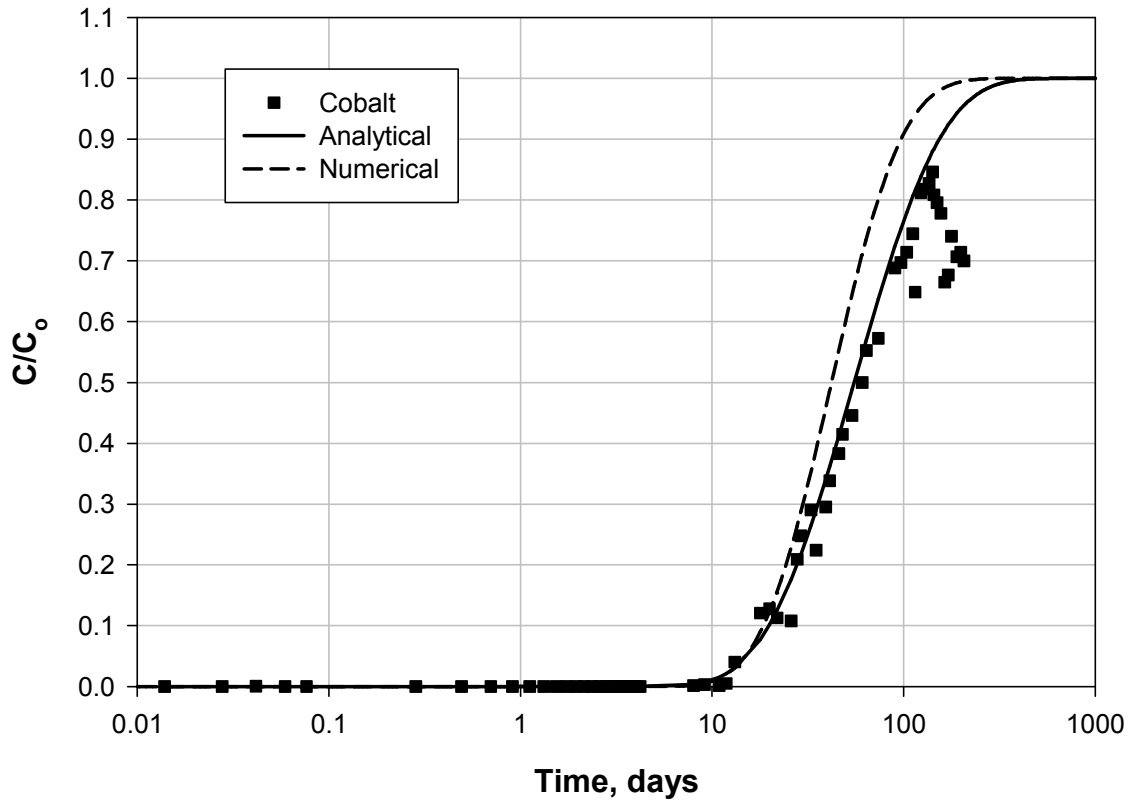

2

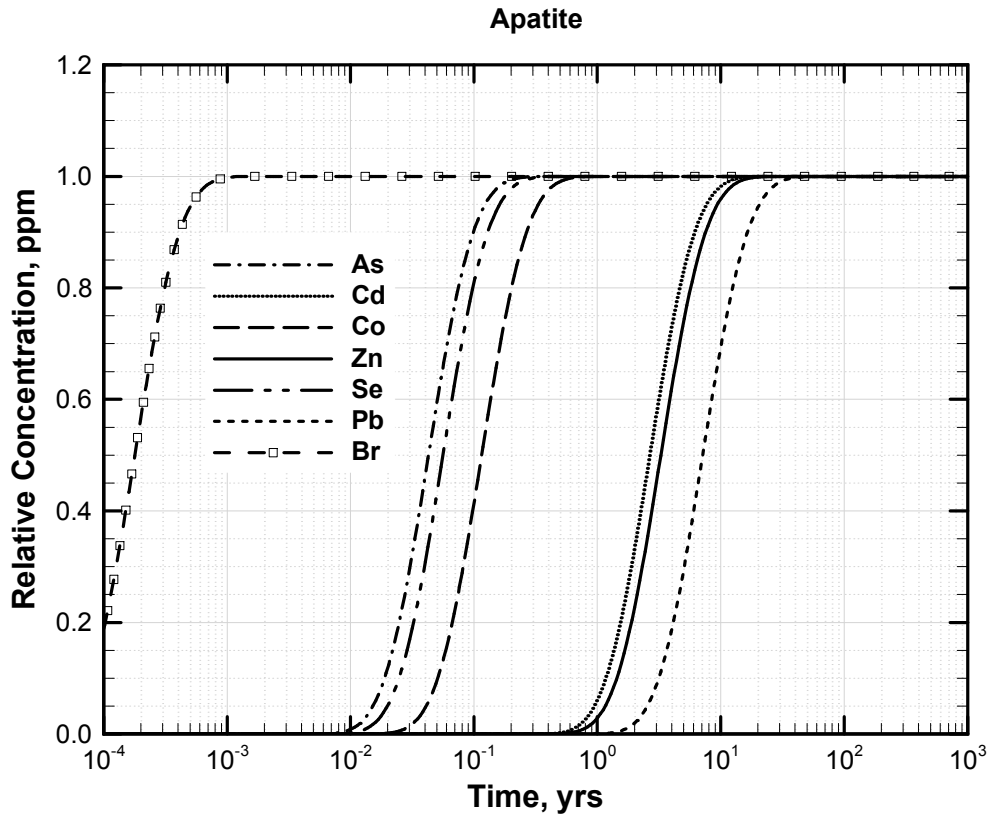3   Exhibit 3. Breakthrough curves for the apatite column.

4

5

Exhibit 4. Analytical and numerical fit to measured cobalt breakthrough data. For both models,

the retardation factor was fixed (based on measured partition coefficient) and the dispersion

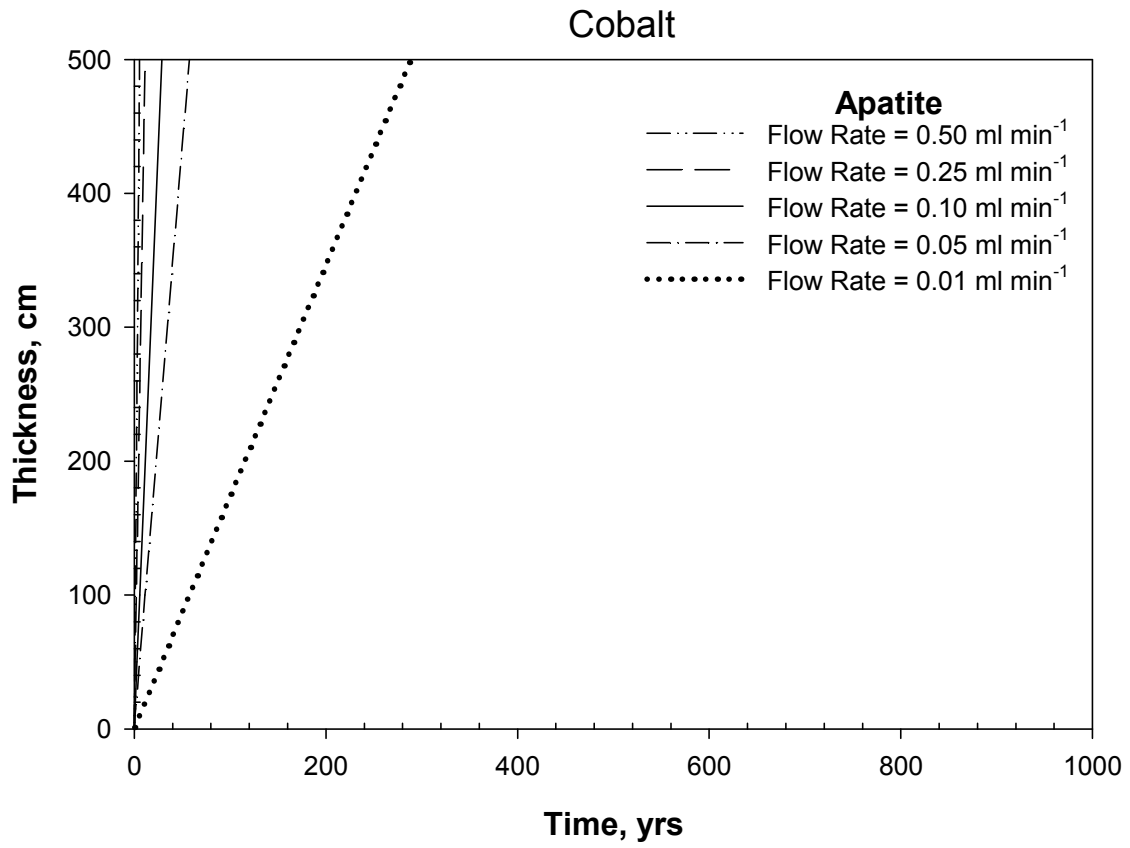coefficient was varied to fit the measured breakthrough data.

1

Apatite

2

3

4 Exhibit 5. Predicted breakthrough curves for the apatite column using numerical model

5 calibrated with cobalt breakthrough data.

6

7

8

Cobalt

Apatite
- Flow Rate = 0.50 ml min^{-1}
- Flow Rate = 0.25 ml min^{-1}
- Flow Rate = 0.10 ml min^{-1}
- Flow Rate = 0.05 ml min^{-1}
- Flow Rate = 0.01 ml min^{-1}

Thickness, cm

Time, yrs

2

3

4   Exhibit 6. Required cap thickness as a function of cobalt breakthrough time for various simulated

5   flow rates.

6

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11

1

Lead

Apatite
Flow Rate = 0.50 ml min^{-1}
Flow Rate = 0.25 ml min^{-1}
Flow Rate = 0.10 ml min^{-1}
Flow Rate = 0.05 ml min^{-1}
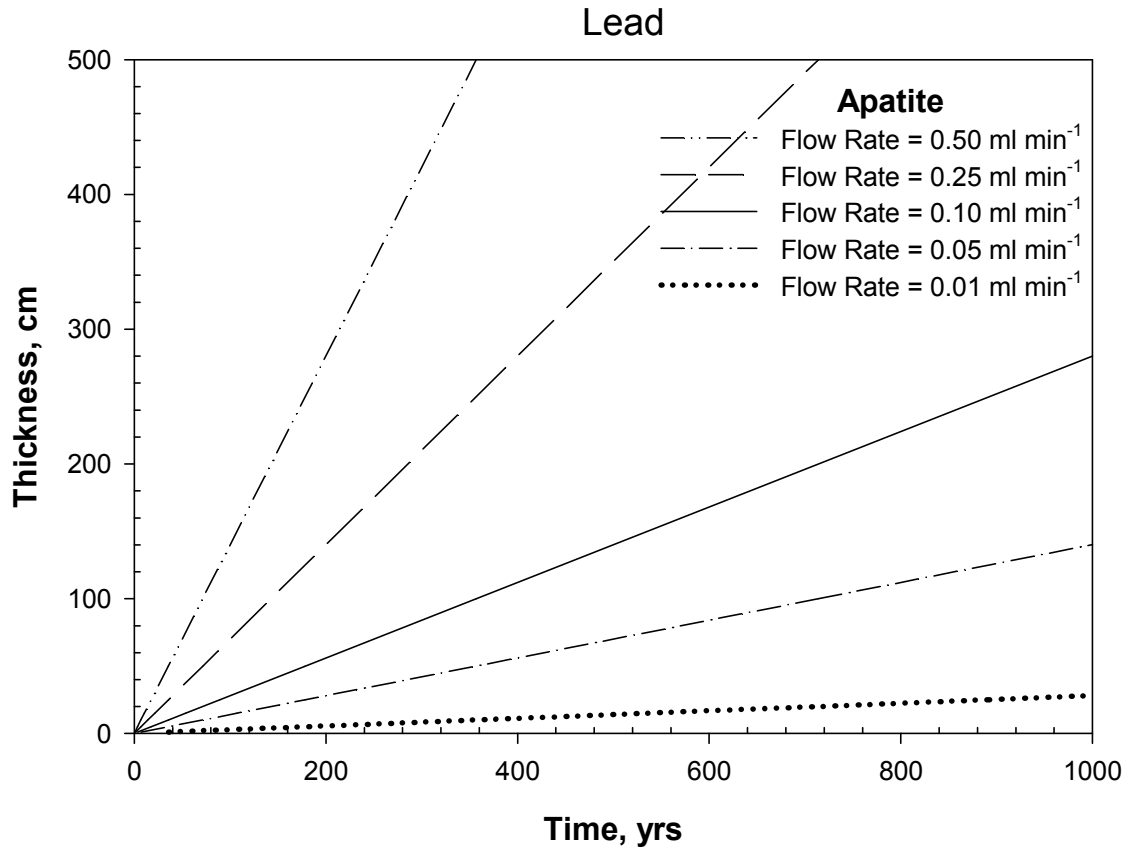Flow Rate = 0.01 ml min^{-1}

2

3

4

5 Exhibit 7. Required cap thickness as a function of lead breakthrough time for various simulated

6 flow rates.

7