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A PRELIMINARY STUDY ON THE APPLICABILITY OF THE TOUGHREACT CODE TO SOUTH AFRICAN COAL SEAM CO_2 STORAGE OPERATIONS: A SIMULATION TOOL THAT CAN MODEL POTENTIAL REGIONAL GROUNDWATER CONTAMINATION RISKS

Tshegofatso. O. P. Mophatlane

Wits University, Johannesburg, South Africa
Tshegofatso.Mophatlane@students.wits.ac.za

ABSTRACT

Carbon dioxide capture and storage (CCS) and underground coal gasification (UCG) are both clean development mechanism (CDM) technologies that have been considered, by the global leadership community, to collectively reflect a significant component of the global transition process towards a renewable energy economy. The hybrid technology has the potential to produce energy from gas, particularly for Integrated Combined Cycle Gasification (ICCG) plants, with lower GHG emissions as well as sequester the CO_2 by-product into the coal and remaining ash underground by injection. South Africa is currently the greatest emitter of the region. One of the hybrid technology's major challenges may be the significant threat that both technologies (CCS and UCG) pose to regional groundwater resources. The aim of this study is to determine the degree of applicability of the TOUGHREACT simulation code to South African coal seam CO_2 sequestration operations. Specific objectives include outlining the possible contamination risks that may threaten regional groundwater-resources quality. The methodology is that of a simple desktop study comparing this project's problem setup with the problem setup in the work of Xu et al. (2006). The Springbok Flats Basin Coalfield in South Africa is used as the case study. The research problem setup involves a shallow aquifer system overlying the coal seam storage site. The results show that, in the event of major CO_2 leakages, the aquifer would be at the risk of hexavalent chromium mobilization and contamination, which may also give rise to precipitation of various mineral phases, depending on the groundwater geochemistry and type of other precipitating mineral phases.

INTRODUCTION

There is an urgent need for catalyzed global carbon emission reduction, as global climate-change effects become more evident with passing time. The exact nature of the contribution of increasing atmospheric CO_2 to long-term effects on global climate is unclear and is still being investigated; however, it is generally accepted that the anthropogenic emission of CO_2 and other greenhouse gases (GHG's) may be the primary cause for the current trend of global climate change (Bryant, 1997; Surridge and Cloete, 2009; Cloete, 2010; Viljoen et al., 2010).

The current trend of global climate change has resulted in gradual increased increase worldwide in Carbon Capture and Storage (CCS) and Underground Coal Gasification (UCG) technology, making them a critical option in the portfolio of clean development mechanism (CDM) solutions for combating climate change (Ashworth et al., 2008; Surridge and Cloete, 2009; Beck et al., 2011).

These technologies have been considered by the global leadership community to collectively reflect a significant component of the global transition process towards a renewable energy economy. The hybrid technology has the potential to produce energy from gas, particularly for Integrated Combined Cycle Gasification (ICCG) plants, with lower GHG emissions, while capturing the CO_2 by-product from the synfuel and storing it in the remaining ash residue underground by means of injection (Shu-quin et al., 2007).

The two CDM technologies are important potential solutions, particularly for developing countries that have significant coal resources, (such as the countries of Southern Africa),

because emissions are expected to increase drastically in such regions (Chandler et al., 2002). The South African economy is currently the greatest GHG emitting economy of the region (Chandler et al., 2002), and its government has committed itself to the goal of being the leader in reducing emissions among the developing-countries community—provided there is adequate financial and research support from the developed-countries community.

One of the hybrid technology's major challenges may be the significant threat that both technologies (CCS and UCG) pose to regional groundwater resources, as illustrated by Figure 1. Previous work by Pruess (2010) and Tsang et al. (2008) has shown that CO_2 storage has the potential to contaminate overlying shallow potable groundwater resources. Carbon dioxide will tend to migrate upwards whenever preferential pathways are available; such as fault zones, bedding planes, joint network or improperly abandoned wells. Migration of CO_2 from storage can also be influenced by cap-rock failure (Rutqvist et al., 2008).

Minimal amounts of CO_2 do not pose a direct threat to potable groundwater (Wang and Jaffe, 2004). More attention should be directed towards evaluating the environmental impacts caused by the secondary effects of CO_2 leakage, namely the geochemical changes caused by the increased CO_2 dissolution in these systems; such as hazardous-trace-metal mobilization (Wang and Jaffe, 2004).

Enabling sustainable development and GHG emissions reduction involves adequate legislature which must be based on a rational, process-based understanding of CO_2 behaviour in the subsurface (Tsang et al., 2002, 2008) and likewise for UCG.

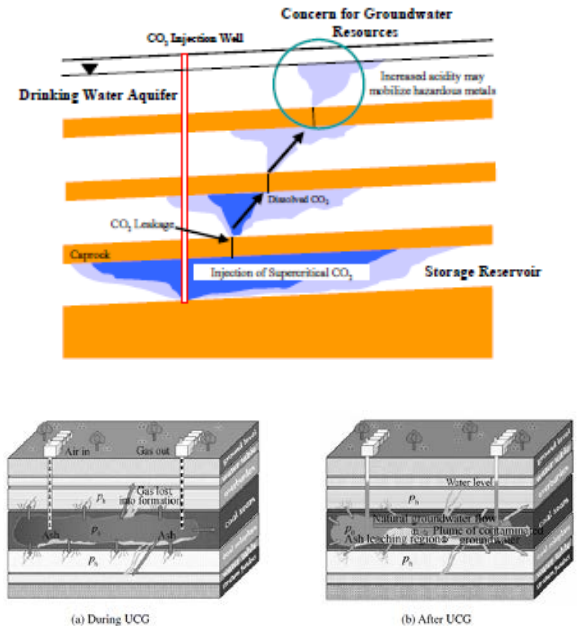

Figure 1. Conceptual model illustrating the possible groundwater contamination risks of CO_2 geological sequestration (Xu et al., 2006) and UCG contamination.

The aim of this investigation is to establish a qualitative rating for the applicability of the TOUGHREACT code to possible future South African coal-seam CO_2 sequestration operations. Specific objectives include outlining the possible hazardous metals that may threaten the groundwater resources of a regional aquifer system

The methodology involved a simple desktop study, which compared this project's problem setup with the problem setup in the work of Xu et al. (2006). The problem setup used in Xu et al. (2006) was modeled on U.S. Gulf Coast sandstone and Ohio carbonate-sandstone.

This research has used the Springbok Flats basin coalfield (Figures 2 -4) and the regional hydro-geological environment as a case study.

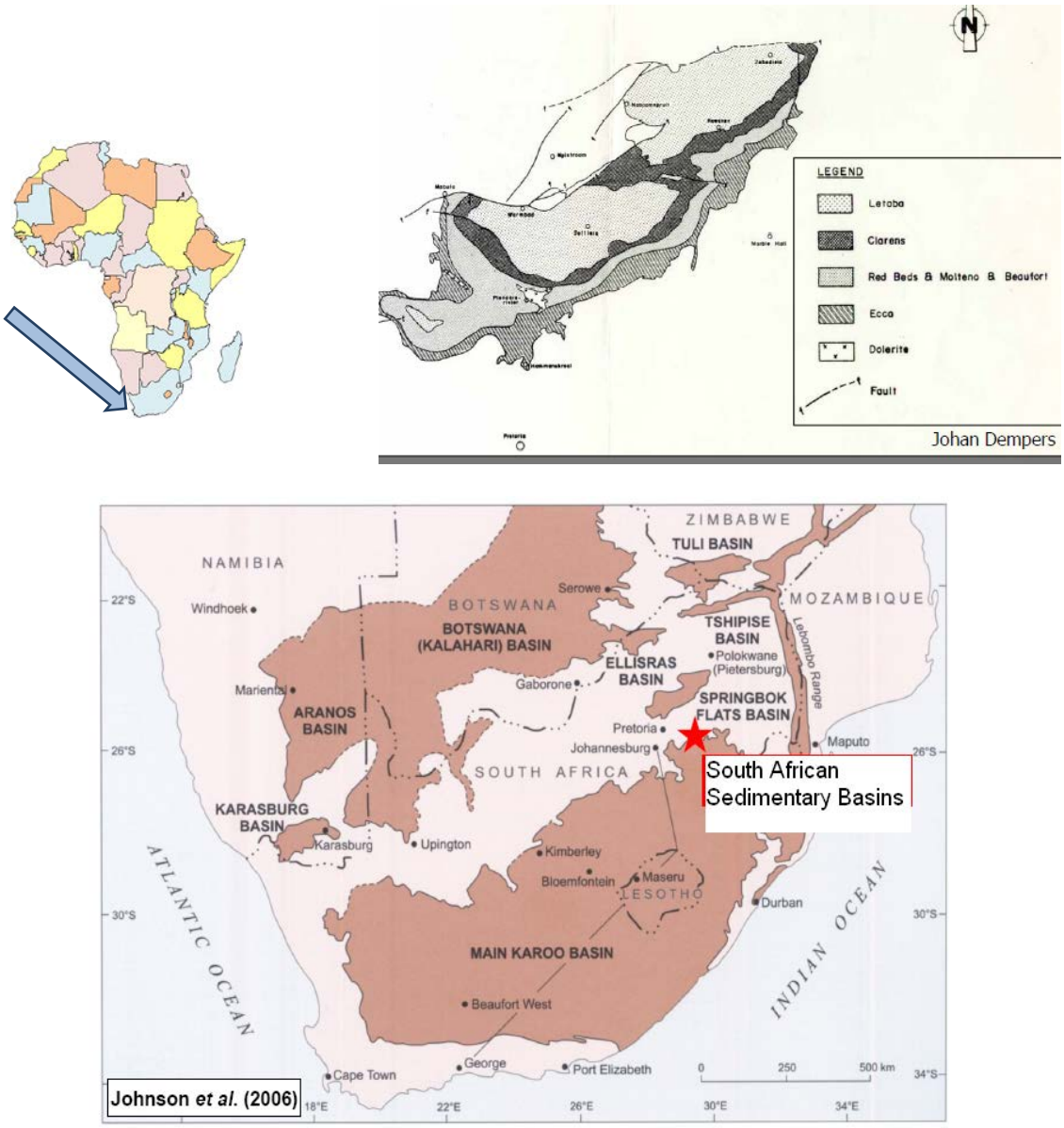

Figure 2. Locality Map of the Springbok Flats basin on the African continent, relative to the other Karoo age basins, illustrating the study area and a geological map of the basin. The geological map illustrates the 3 primary basalt provinces of the Springbok Flats basin

THE STUDY AREA

The problem setup of this paper involves a shallow weathered-zone aquifer system formed by the Clarens Formation Sandstone and Letaba Formation Basalt contact zone, (Figure 3). The coal zone is located within the Hamanskraal Formation and is located ~200 m below the aquifer system (Viljoen et al., 2010).

Topography and Climate

The southern Springbok Flats basin occurs within a relatively flat area with hills at places having elevations between 900 m and 1500 m above mean sea level. The region has a semi-arid climate of hot summers and cold winters and rainfall occurs between October to March receiving 400 mm–800 mm of rain per annum (Rambau, 2011).

Regional Hydrogeology

The primary aquifer of the Springbok Flats is the Karoo Supergroup rocks. The Springbok Flats Basin exists in what has been described as a weathered and fractured aquifer system, and within this aquifer system, groundwater flows through intergranular pores and fractures, in what is regarded as a double porosity system (Rambau, 2011).

The Springbok Flats aquifer system is considered to have high to moderate yielding boreholes, with yields ranging from 3*l*/s to 10 *l*/s making the aquifer system a very significant water source and thus of great importance to the regional communities and municipalities (Rambau, 2011).

The annual recharge of the aquifer system in this region was determined to be 78.10×10^6 m^3/a, with the main source of recharge being rainfall that infiltrates the aquifer in the highland areas such as the Waterberg Mountain (Rambau, 2011). The harvest potential of the aquifer has been given as 25 000 and 50 $000 m^3/km^2/a$, as classified by the map of groundwater harvest potential that was published by the Department of Water Affairs (DWAF, 1998).

The Springbok Flats groundwater has been found to contain high concentrations of fluoride and nitrate, with nitrate particularly abundant in the basalt region, which exists primarily within the northern and central regions of the basin, with minor concentrations in the southern portion (Figure 2). In the northern and central regions, concentrations of nitrate regularly exceed 50 mg/*l* ($N0_x$-N).

Fluoride concentrations have been recorded up to 14 mg/*l*, while total dissolved solides (TDS) of up to 8000 mg/*l* have been measured, but is generally constricted between 200 mg/*l* and 1000 mg/*l* (Hobbs, 1996).

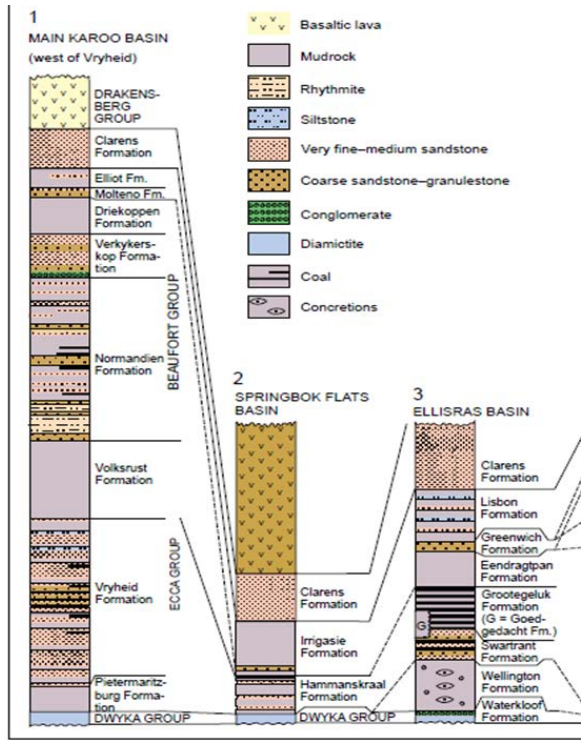

Figure 3. Stratigraphy of the Springbok Flats basin and its correlation with the main Karoo Supergroup in the northeastern part.

Coal Geology

The coalfield has been subdivided based on rank that occurs within the two sub-basins; the shallower northeastern section contains bright, higher-rank coal, while the deeper southwestern section contains raw coal of lower rank. The maximum thickness of Karoo sediments is 1000 m (Viljoen, 2010).

Previous work conducted in the Springbok Flats Basin with respect to CO_2 geo-sequestration has been carried out by Viljoen et al. (2010), who suggest that the possible sites that can accommodate CO_2 geo-sequestration within the basin can only be within the southwestern basin, due to depths there that are greater than 700 m. One of the proposed ideal geological mediums within the sub-basin is the coal zone of the Hamanskraal Formation (Viljoen et al., 2010).

The criteria used to classify the coal zone as a possible site is the potential for coal bed methane (CBM) recovery, the depths of the coal, the 65 m mudrock that has the potential to act as a cap rock, the lateral extent of the coal zone,

and regional dolerite intrusions that could influence CO_2 containment. (Cloete 2010; Viljoen et al., 2010).

There are no mining operations to date within the Springbok Flats coalfield, as this resource has been previously viewed as an unmineable field due to the depth, quality, and high uranium content of the resources (Christie, 1989; Jeffery, 2006; Cloete 2010; Viljoen et al., 2010).

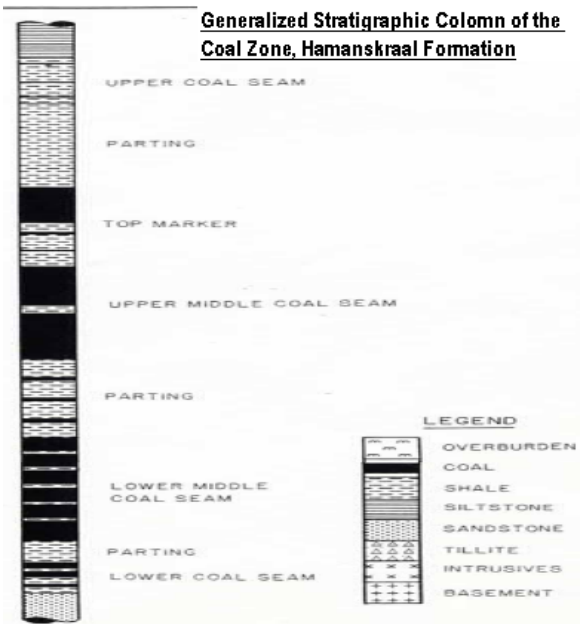

Figure 4. Generalized stratigraphy of the coal zone.

METHODS

Desktop Study

A simple desktop study of the area was undertaken in order to establish the boundaries of the aquifer system, as well as the hydrochemistry and the geochemistry of the aquifer material.

Modeling Approach

This research will only consider conceptual modeling, which will be used as a tool to rate the applicability of the TOUGHREACT code to potential SA CCS operations. The research problem setup is compared to that of Xu et al. (2006), which used the Texas Gulf Coast sandstones and shales as a case study.

A series of chemical kinetics is investigated in order to establish possible dissolution/ precipitation reactions that may take place within the aquifer due to the introduction of CO_2. Since the aquifer system is composed of igneous and sedimentary sediments, it is expected to have a wide range of possible trace metal species that may be dissolved by the carbonated groundwater. Thus, for simplicity, this research has only considered the mobilization of Cr species and the possible oxidation of Cr (III) to Cr (IV), as illustrated below in Figure 6.

The provenance of the sandstone is an important aspect to consider when determining the risk associated with trace-metal mobilization by CO_2 contaminant plumes, particularly for hydrogeological modelling (Xu and Pruess, 2005; Wang and Jaffe, 2003; Xu et al., 2006; Little M. and Jackson R., 2010).

Basalts are formed from fractionated magmas and therefore will usually reflect trace-element variation. The Karoo Igneous Province lavas have been found to be layered, with a high Ti-Zr (low Fe) basalt at the base of the lava flow and a high Fe basalt towards the top of the sequence (Sweeny et al., 1994). The rocks have various compositions of Ti, P, Zr, Nb, Y, La, Ce, Nd, K, Rb, Ba, and Sr.

Table 1 lists the geochemical properties of a basalt province occurring in a sub-basin that has been correlated with the Springbok Flats Basin, the Ellisras (Waterberg) Basin, which lies north of the Springbok Flats Basin (Figure 2 and 3; Kalahari basin) (Barker et al., 2006). There is limited literature on the Springbok Flats basin basalts; however, the Ellisras basin basalts are sufficient for estimating the geochemical properties of the Springbok Flats basalt.

Once CO_2 has entered the aquifer, the pH of the system will drop, and a series of Cr reactions may occur, depending on the groundwater quality and geochemistry of the aquifer material (Wang and Jaffe, 2004).

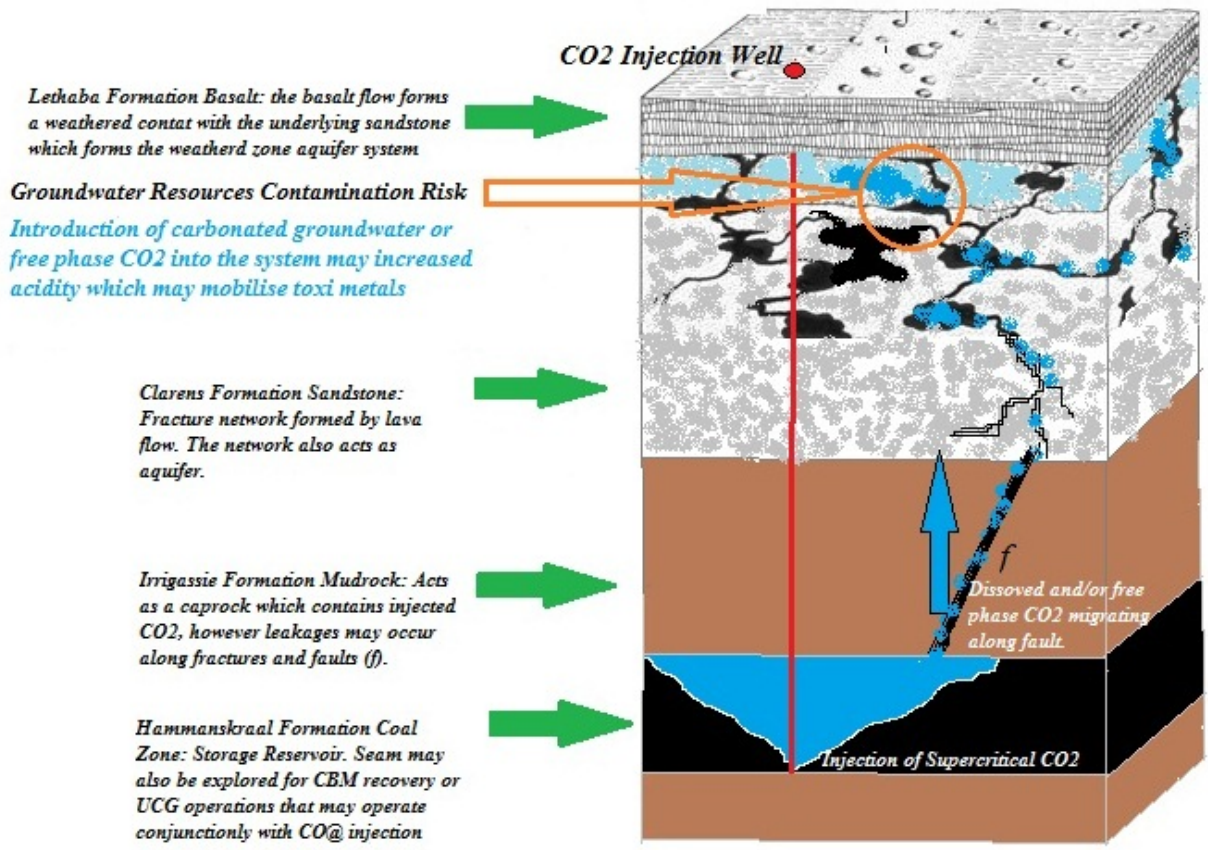

Figure 5. Simplified conceptual model of contamination risks that threaten the weathered-zone aquifer overlying the storage reservoir coal seam. The aquifer sits approximately 200 m above the coal seam

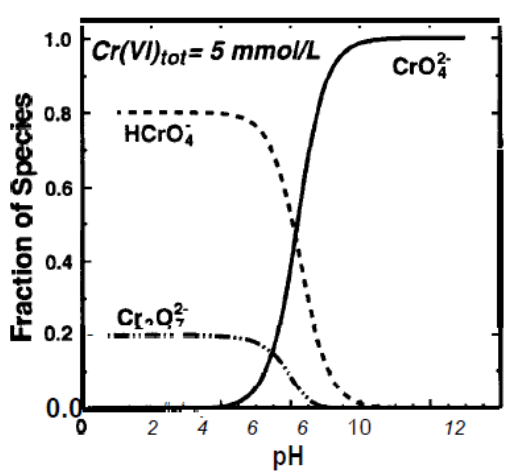

Figure 6. Distribution of Cr (VI) species as a function of pH (Palmer and Puls, 1994).

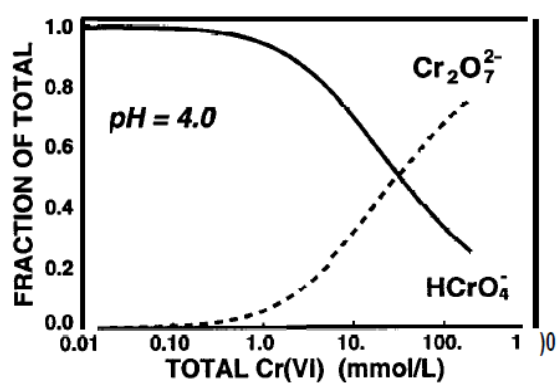

Figure 7. Fraction of bichromate ($HCrO_4^-$) and bichromate ($Cr2O^{2-}{}_7$) at pH 4 as a function of the total Cr (VI) concentration (Palmer and Puls, 1994.

Table 1. Major and minor geochemistry of a basalt lava flow occurring within the Ellisras basin. The boreholes were drilled in the Ellisras basin, Grootgelukke Mine. Major ions (above table) are reported in weight % oxides, while the trace metals are reported in ppm (Reid et al., 1997).

	ELB-4	ELB-15	ELB-20
SiO_2	48.70	50.53	50.43
TiO_2	0.77	0.85	0.87
Al_2O_3	15.22	14.65	14.84
Fe_2O_3	10.21	10.51	9.76
MnO	0.16	0.20	0.20
MgO	7.80	7.42	6.64
CaO	10.35	9.19	10.49
Na_2O	2.19	3.18	1.94
K_2O	0.52	0.67	0.39
P_2O_5	0.11	0.14	0.14
H_2O^-	1.87	1.12	2.15
LOI	1.26	1.96	1.80
TOTAL	99.15	100.42	99.65
Mo	1.4	<0.6	0.7
Nb	4.2	3.8	4.4
Zr	62	63	67
Y	21	22	22
Sr	171	273	192
U	<1.7	<1.6	1.6
Rb	10	11	5
Th	<2.3	<2.3	<2.3
Pb	<2.7	<2.7	2.8
Ba	125	167	126
Sc	30	30	34
Co	48	47	47
Mn	1219	1573	1524
Cr	313	330	335
V	191	210	268
Zn	75	68	77
Cu	41	38	77
Ni	96	83	75
La	12	12	10
Ce	15	14	14
Nd	10	8	9

Hexavalent chromium exists in aqueous state as monomeric ions H_2CrO_4, $HCrO_4^-$ (bichromate), and $CrO^{2-}{}_4$ (chromate), or as the dimeric ion $Cr2O^{2-}{}_7$ (bichromate) (Palmer and Wittbrodt, 1991). The monomeric chromate species are related through a series of acid dissociation reactions:

$$H_2CrO_4^0 \rightleftarrows HCrO_4^- + H^+ \quad ; K_1 \qquad 1$$

$$HCrO_4^- \rightleftarrows CrO_4^{2-} + H^+ \quad ; K_2 \qquad 2$$

The pK values are -0.86 and 6.51, respectively (Alison et al., 1990). Bichromate is the result of polymerization of the monomeric bichromate ions to form the dimer $Cr2O^{2-}{}_7$, where pK_d is -1.54 (Allison et al., 1990). The relative concentration of each of these species depends on both the pH of the contaminated water (Figure 6) and the total concentrations of Cr(VI) (Figure 7).

$$HCrO_4^- + HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + \& \ O \quad ; K_d \qquad 3$$

In the Cr(lll)-H_20 system, Cr(lll) exists predominantly as Cr^{3+} below pH 3.5. With increasing pH, hydrolysis of Cr^{3+} yields $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$;, and $Cr(OH)_4^-$ (Rai, et al., 1987). In the presence of Fe(lll), trivalent chromium can precipitate as a solid solution. If the pH within the contaminant plume is between 5 and 12, the aqueous concentration of Cr(lll) should be less than 1 µmole/L (<.05 mg/L) (Figure 8).

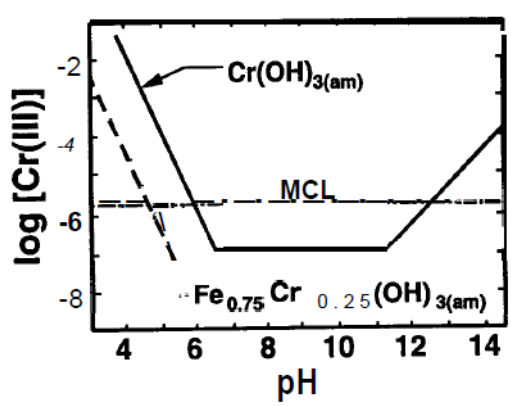

Figure 8. Cr (III) concentration in equilibrium with Cr $(OH)_{3(am)}$ and Fe $_{0.75}$ Cr $_{0.25}$ $(OH)_3$, based on data from Rai et al., (1987) and Sass and Rai (1987), respectively.

Oxidation of Cr (III) to the Toxic Hexavalent Chromium (Cr(VI)) in Groundwater

There are only a few chemical mechanisms for the oxidation of Cr(III) (Bartlett and James, 1979). Only two constituents in the environment

are known to oxidize Cr(III) to Cr(IV): oxygen and manganese dioxides (MnO_2) (Earl and Rai, 1987). Previous work by Schroeder and Lee (1975), and Eary and Rai (1987), has shown that the transformation of Cr(III) by dissolved oxygen is not likely to be a significant mechanism for the oxidation of Cr (III), particularly in groundwater systems.

The other component, MnO_2, has been observed by Bartlett and James (1979); Earl and Rai, (1987); Fendorf and Zasoski (1992) and Risser and Bailey (1992) to have a more significant correlation with Cr (III) oxidation in soils. They found that there is an increase in the rate and amount of Cr (III) oxidation as pH decreases. Experimental results indicate that the oxidation follows Reaction 4:

$$CrOH^{2+} + 1.5\ \delta\text{-}MnO_2 \rightarrow HCrO_4^- + 1.5Mn2+ \quad 4$$

Cr (VI) can be reduced to Cr (III) by a range of various constituents in the environment, such as ferrous (Fe (II)) ion minerals, such as pyrite, reduced sulphur, and soil organic matter (Palmer and Puls, 1994). An example of a Cr (VI) reducing to Cr(III) is given by Reaction 5:

$$HCrO_4^- + 31\%^{2+} + 7H^+ + Cr^{3+} + 3Fe^{3+} + 4H_2O \quad 5$$

The reduction of hexavalent chromium can be limited by a range of compounds such as high sulphate concentrations in groundwater (>2000 mg/L), oxic conditions in the unsaturated zone, high-nitrate concentrations (> 200 mg/L as N). A hydrogeological regime that has high nitrate concentrations will have Cr (VI) plumes persistent in both the unsaturated and saturated zones (Izbicki et al., 2008).

There are several chemical dynamics that involve the reduction of Cr (VI) to Cr (III), also referred to as Cr (VI) attenuation. However, this paper focuses exclusively on the mechanisms that may increase the concentration of Cr (VI) in groundwater, with respect to sequestrated CO_2 leaking into the aquifer.

DISCUSSION AND CONCLUSION

Geological sequestration of CO2 has the potential to mitigate GHG emissions more than any other clean development mechanism (CDM) technology (Ashworth et al., 2008; Surridge and Cloete, 2009; Cloete, 2010; Viljoen et al., 2010; Beck et al., 2011), especially if considered together with coal bed methane recovery and/or underground coal gasification. This technology will therefore represent a significant option for developing countries, particularly South Africa (Beck et al., 2011).

The weathered-zone aquifer of the Springbok Flats basin is a significant shallow aquifer that is extensively used throughout the basin (Heaton, 1985, Rambau, 2011) and represents a resource that would be directly at risk to CO_2 contamination upon commencement of operations. The groundwater resource lies 200m above the coal zone.

The basalt/sandstone sediment aquifer is expected to have a significant Cr content, as illustrated by the Ellisras basalts (Reid et al., 1997), which opens the window to Cr (VI) mobilization and contamination. The probability of Cr (VI) contamination is increased by a decrease in pH (which would be caused by introducing CO_2), the high Mn content of the basalts (Table 1), which bind with oxygen to form MnO_2, which in turn acts as a powerful oxidant to Cr (III), transforming it to the toxic Cr (VI).

The observed high concentrations of nitrate in the Springbok Flats basalt aquifer (Heaton, 1985, Rambau, 2011) is also a major contributor to Cr (VI) contamination (Izbicki et al., 2008).

Such contamination risks should be thoroughly considered and researched in order for adequate site characterization, selection, and policy development, as hexavalent chromium species are extremely toxic—a parameter that should be carefully considered as well as monitored during CO_2 sequestration operations by all stakeholders.

The problem setup of this paper has illustrated that the TOUGHREACT software package has the potential to model contamination risks of CO_2 coal sequestration operations; and thus holds the potential to greatly assist the South African CCS industry in developing a preliminary legislative framework that may be utilized for test injections.

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