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A reappraisal of some Cigar Lake issues of importance to performance assessment

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by

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ABSTRACT

The AECL/SKB Cigar Lake Analogue Study was carried out from 1989 to 1993, the final report being published in 1994. As with many of these international multidisciplinary analogue studies, time schedules are tight and often there is inadequate time to evaluate fully the wealth of scientific data with regard to repository performance assessment issues, one of the major objectives of such studies. Consequently, SKB have allocated time and resources for selected experts, some of whom have been already involved in the Cigar Lake study, to reappraise available data in the light of greater exposure to analogue studies and the development of more realistic models used in performance assessment.

Although several of the areas proved to have been adequately addressed, one of the areas that particularly benefitted concerned radiolysis. In this case a model for radiolysis was developed and tested, significantly narrowing the gap between calculated and predicted oxidant production. Considerable progress was also made in understanding and modelling the initial formation of the deposit under hydrothermal conditions, and using this conceptual model to evaluate the changes that have subsequently occurred under "ambient" repository conditions over geological timescales. Moreover, the physical properties of clay as a potential buffer to groundwater flow and radionuclide migration were addressed with some success.

This Cigar Lake exercise has underlined the advantages of reviewing and reappraising existing analogue data when the dust has settled.

SAMMANFATTNING

AECL/SKB projektet *Cigar Lake Natural Analogue Study* pågick från 1989 till 1993 och slutrapporterades 1994. I likhet med de flesta andra internationella och tvärvetenskapliga studier av naturliga analogier så var tidschemat pressat. Det kan då bli svårt att hinna med en fullständig utvärdering av det omfattande vetenskapliga resultatet med avseende på långsiktig säkerhet för ett slutförvar, som ju är det väsentligaste målet för studien. För att råda bot på detta så har SKB avsatt tid och resurser åt utvalda experter, av vilka flera redan tidigare varit engagerade i Cigar Lake projektet, för att ytterligare utvärdera tillgänglig information och utveckla mera realistiska modeller åt säkerhetsanalysen.

Flera av de utvalda delområdena var redan tillräckligt utförligt behandlade - visade det sig, men i synnerhet radiolysen mådde väl av en grundligare genomgång. Genom att utveckla en ny modell för radiolys så kunde skillnaden mellan beräknad och uppskattad produktion av oxidanter minskas avsevärt. Vi kom även mycket längre på väg mot att förstå och beräkna den ursprungliga hydrotermala utvecklingen av malmkroppen och dess omgivning. Härigenom blev det möjligt att skilja ut de förändringar som även kan ske i ett djupförvar vid normala temperaturer från sådant som redan har bildats hyrotermalt. För övrigt så kunde vi med viss framgång behandla de fysikaliska egenskaperna hos leran som en potentiell buffert mot grundvattenflöde och radionuklidmigration.

Den här Cigar Lake övningen har klart visat på fördelarna med att granska och ompröva befintliga analogdata "när dammet har lagt sig".

CONTENTS

1. INTRODUCTION

The AECL/SKB Cigar Lake Analogue Study was carried out from 1989 to 1993, the final report being published in 1994 (Cramer and Smellie (Eds.), 1994)). As with many of these international multidisciplinary analogue studies, time schedules are tight and often there is inadequate time to evaluate fully the wealth of scientific data with regard to repository performance assessment issues, one of the major objectives of such studies. Consequently, SKB have allocated time and resources for selected experts, some of whom have been already involved in the Cigar Lake study, to reappraise available data in the light of greater exposure to analogue studies and the development of more realistic models used in performance assessment.

All studies indicate that the Cigar Lake uranium deposit has been preserved over very long periods of geological time; major evidence of low temperature radionuclide mobilisation and transport from the uranium orebody or its surroundings is absent. As a result, more focus was put on recent indications of minor radionuclide mobilisation and small changes in mineralogy and geochemistry. To detect and quantify such changes under ambient groundwater conditions, the background extent of the hydrothermal fossil reactions and resultant mineral phases must therefore be reliably known. Consequently, this present study placed emphasisin modelling the genesis of ore formation and emplacement in order to evaluate the mineralogical and geochemical changes that have occurred in the uranium deposit since its formation to the present day.

The origin of the Fe(III) enrichments in the massive clay, adjacent to the ore/massive clay interface, has been the focus of debate. These features, considered to be redox front phenomena, are common to most uranium deposits in the Athabasca basin, and are believed to have played a major role in the hydrothermal process of ore deposition (Hoeve and Quirt, 1987). Alternatively, the iron-rich halo may be post-deposition in origin, resulting from water radiolysis reactions; this is theoretically possible. The origin of the redox phenomenon at Cigar Lake is further studied here by invoking: a) water radiolysis reactions, b) normal water/rock geochemical reactions, and c) hydrothermal reactions.

Radiolysis features as an important process in SKB's assessment of repository performance. Oxidants (e.g. OH-radicals, H_2O_2 and O_2 etc.) generated by radiolysis of water may change the redox conditions of the near-field of a repository. Hydrogen, the stable reductant, which is also generated from radiolysis, is not very reactive at ambient temperatures and is expected to migrate quickly out of the system. The net effect of radiolysis will therefore be one of oxidation. Such changes in the near-field chemistry may influence, in particular spent fuel stability, radionuclide solubility and the buffering capacity of the containing

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bedrock. In all cases mobilisation and transport of radionuclides from the near- to the far-field may be enhanced, and this has important repository performance assessment implications. At Cigar Lake, the large amounts of high grade uranium ore presented the possibility of evaluating the potential influence of radiolysis (alpha, beta and gamma radiation effects) on uranium ore (UO_2) dissolution and the potential transport of radionuclides from the ore, through the surrounding clay halo and into the host sandstone formation (Liu and Neretnieks, 1994).

Present studies set out to address some of the fundamental issues of radiolysis reactions and their potential influence on Cigar Lake observations. In particular: a) a reappraisal of water radiolysis calculations, b) modelling the geometric radiation dose distributions from UO_2 grains, and c) comparison of observed radiolysis evidence from the Cigar Lake orebody with calculated predictions.

The majority of disposal concepts for the safe containment of high-level radioactive waste propose the use of bentonite clay as a packing material placed between the rock wall of the disposal hole and the metal canister which contains the waste. The main objective of the bentonite is to initially delay corrosion of the canister material by restricting groundwater contact from the surrounding bedrock; in the event of canister penetration the bentonite will then serve to retard the mobility and dispersion of radionuclides to the geosphere. The Cigar Lake uranium occurrence, intimately associated with massive clays dominantly comprising illite, therefore offered the opportunity to study at first hand the role of illite (i.e. the worst case repository buffer scenario) in helping to shield the uranium orebody from water-rock interaction and eventual removal since its formation 1.3 Ga ago. Such information could provide valuable input data of buffer material properties to future repository performance assessments. The work presented in this report has concentrated on laboratory measurements of clay physical properties, and comparing the Cigar Lake results to reference clay samples currently being considered in repository construction.

1.1   REFERENCES

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2. THE CIGAR LAKE URANIUM OCCURRENCE

2.1 BACKGROUND

The Athabasca Basin in northern Saskatchewan, Canada, hosts many uranium deposits of hydrothermal origin located along ancient fractures at the unconformity between the Archean basement and the overlying sandstones of Proterozoic age (Fig. 2.1). Several of these deposits have been studied in detail and exploited commercially. There now exists a considerable amount of geochemical data which suggest that the hydrothermal origin of the deposits has resulted from the mixing of U-bearing oxidising solutions and CH_4-rich reducing solutions. Playing a principal role in the origin and evolution history of the ore deposit, especially in the formation and variation of the basement fluids and the hydrothermal alteration processes of the basement rocks in the area, are the basement graphite-rich metapelite rocks (e.g. Hoeve and Sibbald, 1978; Hoeve, 1984; Bruneton, 1987; Percival, 1990; Kyser et al., 1989; Kotzer et al., 1992).

The Cigar Lake uranium deposit is one of the largest in the Athabasca Basin and, in common with the other occurrences, the physico-chemical characteristics of the basement fluids involved in the origin and evolution processes of the deposit are still not well understood. Several questions remain to be answered, for example, the mass transfer processes involved in the formation and evolution of the ore deposit, the migration and mineralisation of uranium and other elements, the presence of a redox reaction front seen in the clay lithology surrounding the orebody, and the subsequent stability of the orebody and surrounding oxide/sulphide/carbonate/silicate mineral assemblages. As the basement fluids and basement metapelite rocks appear to contribute some important controlling and influencing factors to the observed geochemistry of the deposit, greater knowledge of these fluids is critical to understanding the geochemical evolution of the deposit.

2.2 GEOLOGICAL AND GEOCHEMICAL FEATURES

2.2.1 General

The Cigar Lake uranium deposit (Fig. 2.2), located in northern Saskatchewan, is one of many unconformity-type sandstone-hosted uranium deposits of Proterozoic age that characterise the Athabasca Basin uranium province (Fouques et al. 1986; Bruneton, 1985, 1987, 1993).
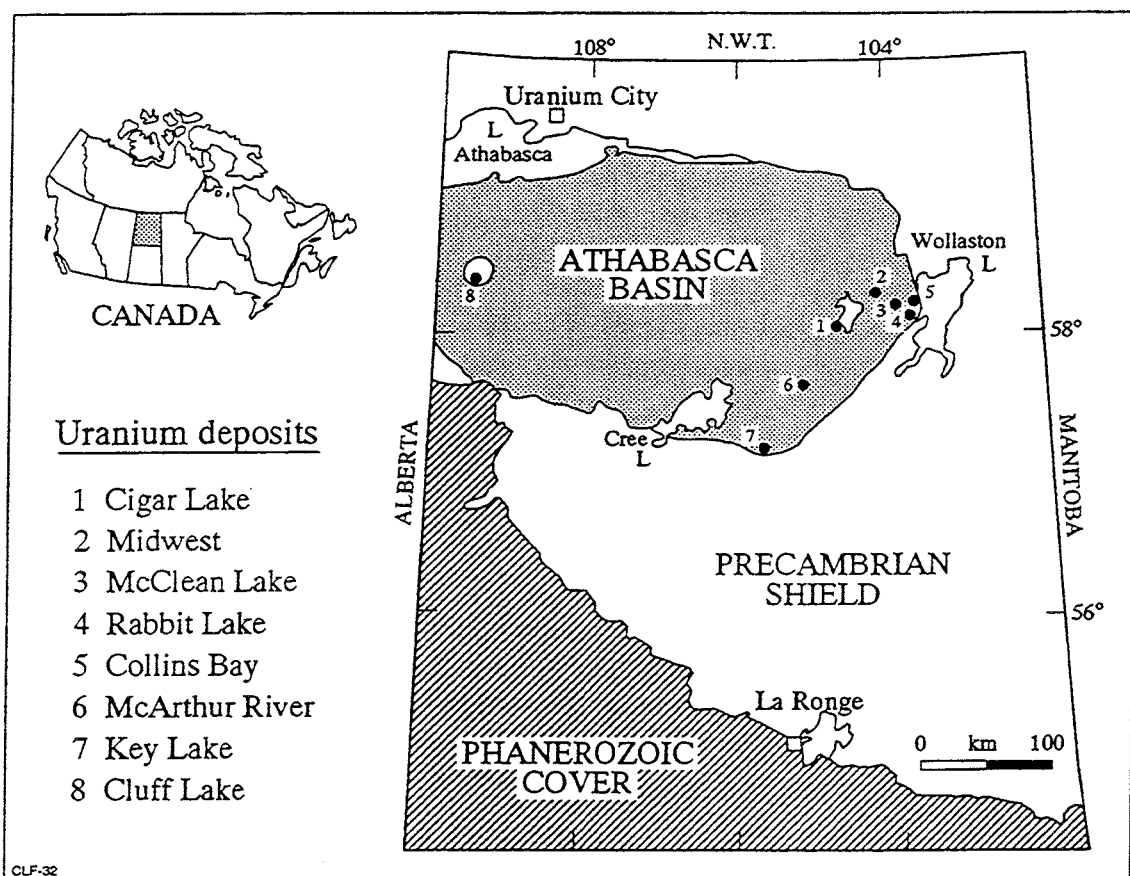
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Figure 2.1:   Location map showing the uranium deposits of the Athabasca
                Basin, northern Saskatchewan, Canada (from Cramer and
                Smellie (Eds.), 1994)

The deposit (at about 430 m depth) occurs at the top of a basement ridge (elevation of 20 m) at the unconformity between the sandstone of the Manitou Falls Formation and the Aphebian graphite-rich metasediment basement known as the Wollaston Group. It comprises mostly uraninite and pitchblende with subordinate coffinite and has been dated to 1.3 Ga (Cumming and Krstic, 1992). The deposit is characterised by a series of geochemical alteration haloes geometrically arranged around the orebody, decreasing in intensity with increasing distance from the ore surface. These haloes comprise a clay-rich zone (mainly illite) of varying thickness (up to 12 m) immediately surrounding the orebody and mostly derived from the hydrothermal alteration of the host sandstones. The clay grades out into altered, friable sandstones and finally to the main Lower Sandstone unit; a highly siliceous horizon (quartz cap) occurs at the interface between the altered sandstone and the competent host sandstones. In addition to these major lithological differences, hydrothermal mineralogical alteration (e.g. illitisation) extends to the bedrock surface, accompanied by geochemical haloes of some trace element concentrations (e.g. U, Cu, Ni, Mo) (Bruneton, 1987).

The unmetamorphosed Proterozoic sediments consist predominantly of micro-conglomeratic sandstones exhibiting a monotonous sequence of medium- to coarse-grained units changing to finer units from near the unconformity to the surface. The coarser grain-sizes also correspond to an increase in the total concentration of heavy minerals (e.g. Fe-Ti oxides, rutile, zircon, monazite) and hence an increase in radioactivity. These unaltered sandstones are also frequently characterised by variable contents of haematite which is reflected in the red/purple/pink colouration of the rocks.

The metamorphic basement below the orebody comprises a steeply south-dipping belt of augen-textured gneiss trending east-west and dipping 50° to 80°. These augen geisses, which coincide with a well defined ridge of basement rocks underlying the mineralisation zone, are surrounded by fine-grained gneissose pelites and calc-magnesian gneisses.

The Cigar Lake area is characterised by a Quaternary overburden of Pleistocene glacial sediments mainly comprising unconsolidated sandy moraine (0-55 m) underlain by a dense till layer (2-4 m).

The hydrothermal alteration around the deposit (both basin sandstones and basement metapelites) is intensive and has been facilitated by an extensive system of fractures extending upwards from a major near-vertical regional fracture zone in the basement trending parallel to the metapelites (Fig. 2.2). According to Bruneton (1987), the hydrothermal alteration of the sandstone displays six concentric zones: B: bleaching zone; Gl: grey alteration zone (marcasite and hydrocarbons are present); Gl+Q: quartz zone (euhedral quartz crystals fill most of fractures); G2: grey alteration zone (illite appears and fractures are strongly developed);
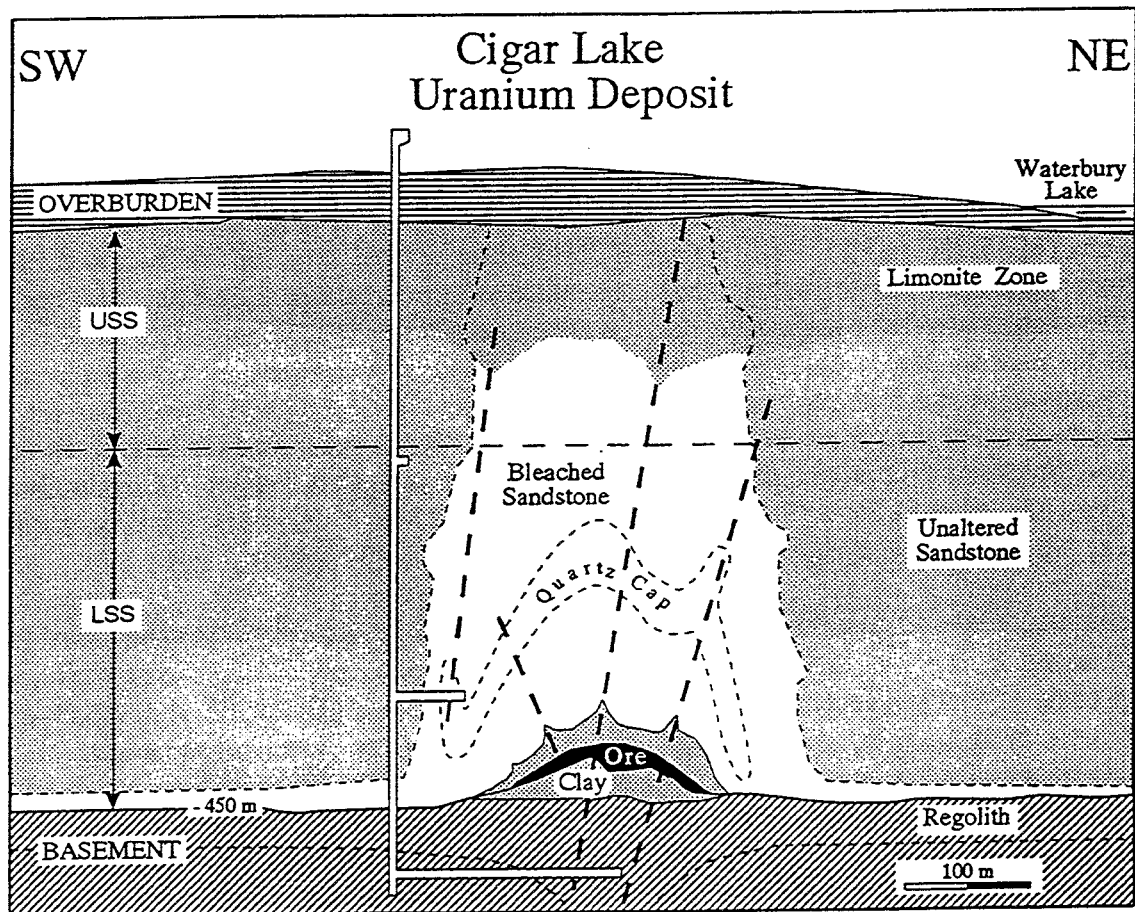
Figure 2.2:   Schematic cross section through the Cigar Lake deposit showing the uranium mineralisation and its host rocks, including the lithologic characteristics related to hydrothermal alteration and weathering. (USS = Upper Sandstone; LSS = Lower Sandstone) (from Cramer and Smellie (Eds.), 1994)

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CL: clay alteration zone (clay content increases progressively towards the orebody, massive irregular soft clay layers or pockets are present, and illite dominates the clay mineral composition); CL+HE: massive clay zone (capping the massive ore zone it is almost entirely composed of clay minerals (mostly illite); haematite and siderite are well developed). In the basement the hydrothermal alteration has totally obliterated the earlier retrograde metamorphic alteration and Pre-Athabasca palaeoweathering, in general producing a totally argillized zone and a partially altered zone.

The intensity of hydrothermal alteration of the basement pelites, and the stability of graphite and pelite mineral assemblages, are dependent upon the permeability and porosity of the basement rocks. In the most permeable structure, i.e. the basement fracture zone located immediately below the richest part of the orebody, all original textures have disappeared, the hydrothermal solutions have altered the rocks to clay-rich assemblages (kaolinite-illite-chlorite), and neither graphite nor pyrite is any longer present. In the less permeable structures, i.e. fractures within the graphitic pelites, original textures are still visible, graphite is only partially altered, silicate minerals (biotite, garnet, amphibole and feldspar) are strongly altered to Mg-rich and Fe-rich illite and Mg-Fe chlorite; pyrite and secondary minerals such as dravite and various phosphates are widespread.

2.2.2   Paragenetic Sequence of Mineralisation

The primary uranium minerals are uraninite (UO_2-U_3O_8) and coffinite ($USiO_4$); these formed coeval with the hydrothermal dissolution of quartz and alteration of the host rocks.

Hoeve and Quirt (1984, 1987) developed a general polymetallic multi-stage model of ore formation for the unconformity-type uranium deposits in the Athabasca Basin. From studies of cross-cutting relationships, mineral paragenesis and radioactive and stable isotopes, three distinct episodes of host rock alteration, mineralisation and remobilisation were recognised. The **first stage** of mineralisation, from 1350-1250 Ma, occurred as the main ore-forming event, generating high-grade ore bodies near the unconformity containing uraninite/pitchblende, Ni-Co-arsenides and sulpharsenides at temperatures around 200°C. The accompanying host rock alterations include: (1) widely spread illitisation and chloritisation in both the basement (from feldspar and mafic minerals) and sandstone (from kaolinite), (2) intensive quartz dissolution, (3) destruction of graphite in the basement, (4) formation of solid hydrocarbon concentrations or "beads", and (5) formation of secondary haematite zone. The **second stage** of mineralisation, from 1100-1050 Ma, resulted in a basin-wide reactivation of diagenetic-hydrothermal activity producing low-grade haloes of pitchblende, Ni-Co and base-metal sulphides at temperatures around 150-200°C. The accompanying host rock alterations are marked by: (1) very extensive bleaching and haematite superimposed

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upon the first stage of hydrothermal activity, (2) emplacement of euhedral quartz veins, (3) formation of tourmaline (dravite), siderite, calcite, geothite, and berthierine, (4) graphite destruction, and (5) hydrocarbon formation. The **third stage** of mineralisation, from 300-250 Ma, resulted in uranium remobilisation producing an assemblage of sooty pitchblende, coffinite, haematite and minor sulphides at temperatures around 50°C. The accompanying host rock alterations were characterised by intensive kaolinitisation. Fluid inclusion studies indicate that the first two stages of mineralisation are associated with the mixing of a basement fluid and a high-grade diagenetic brine, while the last stage is related to meteoric water reactions from which the retrograde-diagenetic kaolinite has formed.

Bruneton (1987) also proposed a three-stage model of ore formation which is in general agreement. The first stage of mineralisation represents radiating pitchblende and euhedral uraninite, with coexisting Ni-Co arsenides, sulpharsenides, and Ni-Co-Fe sulphides; the second stage of mineralisation represents two pitchblende-bearing phases, one with secondary Ni-Co arsenides, sulpharsenides and Fe-Cu sulphides, and the other with only Fe-Cu sulphides; the third stage of mineralisation represents the replacement of pitchblende by Fe-oxides and hydroxides.

Table 2.1, after Bruneton (1987), shows a generalised paragenetic scheme of mineralisation and hydrothermal alteration produced by the Cigar Lake ore formation processes.

Table 2.1: Simplified paragenesis of mineralisation (Bruneton, 1987)

	Mineralization				Gangue
Stage I	Uranium oxide UO₂				
	- radiating facies (pitchblende)				Fe-rich illite
	- euhedral facies (uraninite)				Mg-rich illite
	—brecciation—				
	:Arsenides, sulpharsenides, sulphides				
RAMMELSBERGITE	NiAs₂	PYRITE	FeS₂		
NICCOLITE	NiAs	MARCASITE	FeS₂		
GERSDORFFITE	NiAsS	BRAVOITE	(Ni, Co, Fe)S₂		
COBALTITE	CoAsS				
GLAUCODOT	(Co,Fe)AsS				
	—fracturing—				Siderite
Stage II	Uranium oxide UO₂				"Ferri-kaolinite"
	PITCHBLENDE FACIES				Sudoite
1. Secondary arsenides, sulpharsenides, sulphides		2. Sulphides			
PYRITE	FeS₂	PYRITE	FeS₂		
MARCASITE	FeS₂	MARCASITE	FeS₂		
BRAVOITE	(Ni, Co, Fe)S₂	(BRAVOITE)	(Ni, Co, Fe)S₂		
(SMYTHITE)	(Fe, Ni)₃S₄	(SMYTHITE)	(Fe, Ni)₃S₄		
		(CHALCOPYRITE)	(Cu, Fe)S₂		
CHALCOPYRITE	(Cu, Fe)S₂	(GALENA)	PbS		
(BORNITE)	Cu₅FeS₄	(SPHALERITE)	ZnS		
(DIGENITE)	Cu₉S₅				
(CHALCOCITE)	Cu₂S				
(COVELLITE)	CuS				
GALENA	PbS				
SPHALERITE	ZnS				
(JORDISITE)	MoS₂				
(CLAUSTHALITE)	PbSe				
	—fracturing—				Carbonates (calcite)
Stage III	Uranium oxide and silicate				
	PITCHBLENDE - COFFINITE				
	Iron oxides and hydroxides				

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2.2.3 Compositional Features of the Cigar Lake Uraninites

General petrographic descriptions of the Cigar Lake massive ore body are few, the available data being mostly restricted to the detailed mineralogy and chemistry of single grains and aggregates (e.g. Cramer et al., 1994; Janeczek and Ewing, 1994). The main chemical features have been summarised by Bruno and Duro (1995), based on chemical and mineralogical determinations on uraninite samples from Cigar Lake reported by Janeczek and Ewing (1992 a,b); analyses of the most important uranium phases are given in Table 2.2. The following general features can be expressed:

* Despite its massive appearance, the uraninite samples show a remarkable textural and chemical heterogeneity indicating dissolution and subsequent infilling by chalcopyrite. The textural and chemical analyses indicate the replacement of a Pb-rich uraninite by a Pb-depleted uraninite with increasing contents of Si and Ca in the altered grains. Coffinitisation appears to be concurrent to this alteration process.

* The Pb-depletion processes have been episodic rather than continuous, and the major Pb mobilisation events are considered to correspond to: a) the major mineralisation which occurred 1.3 Ga ago, b) illite-haematite precipitation at around 0.9 Ga ago, and c) further hydrothermal activity some 0.3 Ga ago accompanied by subsequent coffinitisation.

Table 2.2: Electron microprobe data (wt.%) for uraninite, altered (1) and unaltered (2), and coffinite (3), from the Cigar Lake deposit (selected from Janeczek and Ewing, 1992 a,b).

	1	2	3
UO_2	84.77	81.09	67.23
SiO_2	2.71	0.36	13.31
ZrO_2	0.60	0.31	0.00
PbO	1.39	11.46	0.06
CaO	2.28	1.54	0.68
FeO	0.75	0.38	0.00
Y_2O_3	0.09	0.70	0.00
La_2O_3	0.00	0.11	0.00
Ce_2O_3	0.00	0.09	0.00
Gd_2O_3	0.00	0.10	0.00
Tb_2O_3	0.00	0.75	0.00
Al_2O_3	0.33	0.00	0.72
P_2O_5	0.16	0.19	0.00
Total	93.08	96.31	82.91

* The unaltered Pb-rich uraninites have a larger U(VI) content than the Pb-depleted varieties. The calculated U(VI)/U(IV) stoichiometries for these phases are: unaltered uraninite ($UO_{2.23}$ containing an average PbO content $x_{PbO} = 0.13$); altered uraninite ($UO_{2.16}$ with a PbO content $x_{PbO} = 0.02$). Coffinites did not contain any significant PbO (Table 2.2).

This information, in common with other data on the genesis of the uranium ore deposit, is consistent in indicating that a release of roughly 7% of uranium as U(VI) has occurred in the last 0.8 Ga (disregarding the influence of lead).

2.3 ORIGIN AND EVOLUTION: SIMULATION OF GEOCHEMICAL PROCESSES

2.3.1 Introduction

The Cigar Lake Analogue Project was mainly focussed on the study and understanding of geochemical processes which had occurred, or are presently occurring, under ambient groundwater conditions. The hydothermal origin of the Cigar Lake uranium occurrence 1.3 Ga ago was therefore of little apparent importance to the interpretation of these data; the hydrothermal character of the uranium deposit basically constituted the underlying geology, mineralogy and geometry of the system studied. Before the completion of the Cigar Lake Analogue Project, however, the potential significance of understanding the origin of the Cigar Lake deposit was increasingly realised, with particular reference to the following issues of importance:

1) All studies indicate that the Cigar Lake uranium deposit has been preserved over very long periods of geological time; major evidence of low temperature radionuclide mobilisation and transport from the uranium orebody or its surroundings is absent. Consequently, more emphasis was put on recent evidence of minor radionuclide mobilisation and small changes in mineralogy and geochemistry. To detect and quantify such changes under ambient conditions, the background extent of the hydrothermal fossil reactions and resultant mineral phases must therefore be reliably known.

2) The origin of the Fe(III) enrichments in the massive clay, adjacent to the ore/massive clay interface, has been the focus of debate. These features, considered to be redox front phenomena, are common to most uranium deposits in the Athabasca basin, and are believed to have played a major role in the hydrothermal process of ore deposition (Hoeve and Quirt, 1987).

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Alternatively, the iron-rich halo may be the product of water radiolysis reactions; this is theoretically possible and is addressed in Chapter 4, Section 4.1.

3) In most analogue circles the Cigar Lake uranium occurrence is considered one of the most "complete" analogues to a high-level radioactive waste disposal site. However, criticism to its widespread use has come from some quarters. The main objection is that there exists a nearby occurrence (e.g. Close Lake) located at similar depths and has a similar geometry but, in contrast, contains very little uranium. The inference is that the uranium has been removed over geological timescales.

There are two responses to this critique. One, considering all things equal, is it not more constructive to understand why Cigar Lake has been preserved, rather than focus on the negative inference of Close Lake? Secondly, perhaps Close Lake never comprised a large uranium deposit due to formation under contrasting geological and hydrothermal physico-chemical conditions to those which gave rise to Cigar Lake. On balance, however, and given the necessary resources, it would be well worthwhile to study more quantitatively Close Lake in order to allay such criticisms.

These three issues may be partly resolved by being able to reliably simulate and quantify the hydrothermal geochemical processes involved in the origin and evolution of the Cigar Lake uranium occurrence. Only by achieving this, is it possible to separate and quantify subsequent low temperature reactions and processes which have been superimposed on the fossil hydrothermal fabric.

2.3.2   **Model Development and Application**

The CHEMSAGE computing package, using the technique of Gibbs free energy minimisation, offers a thermodynamic approach for studying heterogeneous metallurgical systems (Eriksson and Hack, 1990). This package has been modified to a geochemical/geoenvironmental version, named CHEMGEO by Shi et al. (1993a; 1996), designed to study the complicated hydrothermal processes and geochemical phenomena relevant to the origin and preservation of the Cigar Lake uranium deposit. Using this approach it has been possible to use effective and reliable models, methods, and databases for multicomponent fluids, aqueous solutions and solids, to thermodynamically and kinetically simulate the heterogeneous reactions involved in the natural system at Cigar Lake (Shi et al., 1993b, 1995).

CHEMGEO has been used to perform theoretical simulations of six major

geochemical issues related to Cigar Lake:

1) The hydrothermal/metamorphic stability of graphite and various graphite-bearing oxide-, sulphide-, carbonate- and silicate-assemblages that characterise the Archean basement complex underlying the uranium deposit, and which have participated in the ore-forming processes at elevated P-T-X conditions.

2) The hydrothermal stability of the various uranium-bearing minerals and their oxide-, sulphide-, carbonate- and silicate-bearing assemblages produced at elevated P-T-X conditions during the ore-forming processes.

3) Hydrothermal stability of the important clay minerals (e.g. illite, smectite, chlorite, sudoite and kaolinite) produced during the ore-forming processes, and the buffering capacity of these clay assemblages in the various oxide-, sulphide-, carbonate- and silicate-bearing assemblages during hydrothermal interaction of basement and overlying sandstone rock-forming minerals with different aqueous solutions.

4) Simulation of metamorphic and hydrothermal interaction between basement graphitic metapelites and basement fluids. Emphasis was placed on the formation and evolution of basement fluids, on the P-T-X-S-W relations of basement reactions, and on the mineral assemblages of the various basement rocks.

5) Simulation of unmineralised regional sandstone equilibrium mineral assemblages and the heterogeneous equilibria associated with their hydrothermal interaction with aqueous solutions of various initial bulk compositions. These simulations were carried out at P-T-ω conditions corresponding to diagenesis and hydrothermal alteration of the sandstones.

6) Simulation of two-fluid mixing, i.e. interfacing of mineralising fluids from the basement with the aqueous solutions circulating in the overlying sandstone formations, to account for ore formation and the associated alteration mineral assemblages in the surrounding sandstones.

2.3.3   Summary of Results

Essentially, basement fluids, mobilised by hydrothermal activity during metamorphism, have reacted with the Archean basement rocks. The presence at Cigar Lake of an ancient sub-vertical, large-scale lineament

structure, has enabled these fluids to progress and react with the near-vicinity rock units to the top of the basement complex. These fluids are reducing when they emerge from the basement into the U-rich brine system of the overlying sandstone basin. As these two fluid systems mix, the uranium precipitates forming the bulk of the ore deposits. Following the main uranium precipitation phase, hydrothermal reactions continued at lower temperature to pervade upwards and outwards into the overlying sandstones, facilitated by a system of sub-vertical fracturing, producing a roughly symetrical alteration halo around the ore deposits.

Basement Reactions

Graphite, present mostly in graphite-rich basement metapelites (3-10% carbon), has played a principle role in the origin and evolution history of the ore deposit, especially in the formation and variation of the basement fluids and their strongly reducing character. Model simulations (Shi et al., 1993b) have shown that under the P-T-X conditions of the Cigar Lake deposit environment, the reaction mechanism of graphite is mainly reduction, resulting in methane (instead of CO_2) with lesser amounts of hydrogen sulphide. With these two species dominating the hydrothermal basement fluids, and the graphite always being stable in the interaction system, very reducing and high pH conditions existed in the Cigar Lake basement rocks.

Basement reactions with these very reducing fluids were shown to result in a continuous alteration of the various types of basement rocks. Alteration commences at around 350-300°C with the dissolution of quartz, biotite, garnet and the formation of calcite, sudoite, chlorite and micas; around 250-200°C dissolution of graphite and recrystallisation of illite to smaller grain sizes occurred, followed by the formation of pyrrhotite; at lower temperatures around 180-150°C the illites became larger in size and some replacement by smectite to form illite-smectite mixed layers occurred. Pyrite at these lower temperatures may also form.

In these reactions, the dissolution reaction equilibria of biotite, K-feldspar, plagioclase, quartz and graphite dominate the aqueous solution equilibrium, and the formation of clay, carbonate and sulphide minerals, and CH_4/CO_2, control the speciation and pH-Eh conditions.

These simulations are supported by observations recording the extensive hydrothermal interaction during the main fluid-mixing mineralisation stage (described below) and during subsequent episodes of hydrothermal activity. This has resulted in the basement metapelite rocks (geochemically the most important unit) showing a complete disappearance of graphite, intensive dissolution of quartz, and co-existence of uraninite, chlorite, illite, smectite, pyrite and anhydrite in the first few metres underlying the unconformity. With increasing depth, the stability of graphite increases and quartz becomes increasingly more

stable together with chlorite, illite, smectite and pyrite.

Source of Uranium

The sandstones overlying the metamorphic Archean basement complex are fairly homogeneous and characterised by a simple mineral assemblage, i.e. dominantly quartz (>80%) with subordinate mica, kaolinite, illite-smectite, chlorite, haematite, rutile and sphene. Prior to hydrothermal activity, most uranium was probably matrix bound and labile. Some radioactive accessory mineral phases (e.g. monazite, zircon) tend to be concentrated in thin bands which increase towards the bottom of the sandstone sequence, becoming particularly concentrated in the underlying regolith horizon.

At the onset of hydrothermal activity the sandstone fluids were characterised by high Eh, low pH and high salinity (Pagel, 1975); this resulted in brines with a great capacity to alter the rocks and to leach uranium from the sandstones and the basement regolith which is considered to be the major uranium source for ore formation (M. Pagel, per. comm. 1994).

It has also been demonstrated that the dominant complexes controlling the hydrothermal transport of uranium through the sandstones were the UO_2^{2+}-chloride and -hydroxyl complexes and U^{4+}-hydroxyl complexes; in some cases sulphate and carbonate complexes of UO_2^{2+} may also have contributed significantly.

Two-fluid Mixing and Ore-forming Processes

The simulations have shown that substantial uranium mineralisation occurred at pressures of 1-2 kbar and at around 200°C, as the basement fluids (relatively low Eh, high pH, low salinity, high T-P, high CH_4-H_2S contents) encountered basin brines (relatively high Eh, low pH, high salinity, low T-P, high $Cl^-/CO_2/HCO_3^-/SO_4^{2-}$ contents and high UO_2^{2+} concentrations). Mixing of these two fluids probably occurred in a permeable zone near the vicinity of the large-scale fracture intersection with the basement and sandstone unconformity. The primary mineralisation produced only uraninite (as the U-bearing phase) in equilibrium with graphite, pyrite/pyrrhotite, magnetite and siderite; haematite is shown to be unstable in the presence of such a mineral assemblage.

At lower temperatures in the orebody (150-100°C) haematite became stable with pyrite and siderite; pyrite and siderite precipitated with further uraninite in the orebody, but haematite spread pervasively through the orebody, into the surrounding massive clay, and out into the overlying sandstones. This may be the mechanism that has given rise to the widely developed hematite haloes in the clays adjacent to the ore/massive clay

interface, and also the heavy hematite coatings along fine fractures and fissures transecting some of the massive clay horizons.

At still lower temperatures, haematite became stable in the presence of illite, smectite and other low temperature minerals. At this juncture the hydrothermal system was characterised by somewhat higher pH-Eh values such that the surfaces of some of the uraninite grains became oxidised, rounded and embayed; magnetite and siderite either disappeared or recrystallised and some of the coffinite was effected by the later uranium remobilisation and mineralisation.

The simulations demonstrate that the stability of graphite and pyrite/haematite and equilibrium speciation of carbon and sulphur components in the hydrothermal interaction system, are of paramount importance to explain the observed features of the mineralisation. Also shown is the stability of the various U-bearing minerals under hydrothermal conditions at the basement unconformity. Furthermore, the stability of the clay phases in the hydrothermal system appears to be the key controlling factor in the formation of the orebody and the surrounding alteration haloes. The buffering capacity of the Cigar Lake clay minerals is apparent by the preservation of the relatively stable physico-chemical properties (i.e. pH-Eh conditions; aqueous speciation; fluid fugacities) of the hydrothermal interaction system. This is evident from:

- the high stability of such clay minerals over the whole range of *T-P* conditions subsequent to ore formation,

- the co-existence of clay minerals with not only the uraninite-pyrrhotite-magnetite-siderite assemblages, but also the haematite-bearing assemblages, and

- the wide range of chemical and mineral compositions of clay minerals (especially illite and chlorite).

Hydrothermal Alteration of the Sandstones

Primary basin sandstone assemblages consist of mica, illite-smectite, chlorite, haematite, kaolinite, rutile and sphene. The stability of haematite in the original sandstone was confirmed by the coupled Fe-C-S-O redox equilibrium in the system. The degree of alteration and leaching of the sandstones during hydrothermal activity depended mainly on: a) the initial bulk composition of the aqueous solutions, b) the temperature, c) the rock/fluid ratio, and d) the pressure, of the system. The modelled simulations support the petrographical observations that the sandstones have been hydrothermally altered and leached to varying extent around the uranium orebody, producing a series of alteration haloes of decreasing intensity away from the mineralising two-fluid mixing source at the basement/sandstone unconformity.

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Near the orebody the dissolution and alteration of original minerals (quartz-biotite-feldspar-mica-chlorite-kaolinite) has been intensive, and in most cases mica, biotite and feldspar have been completely altered to clay minerals; haematite and chlorite may be unstable under some circumstances whilst smectite and illite are normally very stable.

Essentially the following major sequence of simulated processes have affected the host sandstone formations:

- strong hydrothermal alteration of fractured lower basin sandstones coeval with interaction of the initial, intensive two-fluid mixing mineralising phase,

- later continuous mineralisation/remobilisation resulted in the formation, evolution and zoning patterns of the alteration haloes around the orebody,

- formation of the massive clay halo characterised by strong dissolution of quartz, mica and kaolinite, and intensive formation of illite together with uraninite,

- further alteration at lower temperatures (175-100°C and lower) whereupon haematite, possibly in association with uranium, was redistributed adjacent to the massive clay/ore interface forming a distinct halo,

- the pH-Eh conditions, equilibrated mineral assemblages (especially illite-smectite-chlorite-kaolinite clay and haematite-pyrite minerals) and aqueous speciation (especially of C-S-Fe-U equilibria), show variable ranges along a profile extending from the orebody, through the alteration haloes and up into the less altered host sandstones.

2.3.4   Conclusions

The main conclusion to this study has been the success in simulating:

1) The composition of the basement hydrothermal fluids,

2) The alteration mineralogy resulting from hydrothermal interaction of the basement fluids with the basement rock units,

3) The composition of the sandstone brines,

4) The formation of the uranium orebody by mixing hydrothermal basement fluids with the sandstone brines,

5) The alteration mineralogy around the orebody resulting from the mixing of hydrothermal basement fluids and the sandstone brines, and

6) The controlling factor of the clay phases in the formation of the orebody and the surrounding alteration haloes.

Furthermore, the simulations have addressed the major issues outlined in Section 2.1. For example:

- The close agreement between the simulations and the observed features of the Cigar Lake uranium deposit provides a more reliable mineralogical and geochemical base from which to interpret the significance (if any) of more recent, low temperature rock/water interaction processes.

- The presence of haematite concentrations in the clay halo adjacent to the orebody/clay interface does not necessarily require hydrothermal conditions to be formed. However, it has been demonstrated by theoretical calculations that it may very well be generated by low temperature oxidation reactions resulting from late-stage ore-forming hydrothermal processes.

- The importance of graphite in the origin and evolution of the Cigar Lake uranium deposit has been demonstrated. In the absence of any published mineralogical and geochemical data from the nearby Close Lake, and assuming that an uranium orebody has not been leached subsequent to ore formation, it can be speculated that either: a) there was insufficient graphite in the underlying basement rocks to produce the very reducing hydrothermal fluids necessary for massive uranium precipitation, and/or b) the overlying sandstones were barren, i.e. already leached of most of their uranium prior to hydrothermal activity.

2.4 ORIGIN AND EVOLUTION: AN ALTERNATIVE APPROACH

Bruno and Duro (1995) provide an alternative approach in discussing the origin and evolution of the Cigar Lake uranium deposit, in particular the genesis of the red haematite/oxyhydroxide halo at the massive ore/clay contact. They initially consider the more global evolution of Cigar Lake, where there is a unique palaeorecord, in establishing early Precambrian atmosphere boundary conditions at the onset of ore formation, and then tracing the geochemical development of the Athabasca Basin through time before focussing on the fine detail of the deposit to test their hypothesis.

Fortuitously, most of the scientific evidence related to the genesis and evolution of the Precambrian atmosphere is to be found from studies of the Athabasca Basin (Holland, 1984; Holland et al., 1995). It was therefore possible to constrain one of the major geochemical parameters of the system (pCO_2) at the time of ore formation and subsequently estimate the initial oxygen fugacity. This indicated a geochemical environment which was much more oxidising than that actually derived from measurements of the ore body itself. The recent work of Raffensperger and Garven (1995 a,b), which involved a coupled hydrothermal/hydrochemical dynamic model to explain uranium genesis and evolution within the Athabasca Basin over geological timescales, was used to establish some of the main geochemical parameters at the conclusion of ore formation at Cigar Lake. In particular, the precipitation of the various Fe- and U-bearing phases and the resulting redox conditions within the ore body. Bruno and Duro (op. cit.) conclude that at the termination of ore formation (approx. 0.5 Ma after the onset of the process) the prevailing redox condition within the ore body was mildly oxidising. These data essentially corresponded closely to the initial calculations based on palaeoatmospheric data.

These global scale calculations were then compared to detailed mineralogical data from the uraninites constituting the orebody. These data, which are based on the work of Janeczek and Ewing (1992 a,b) and summarised in Section 2.3, indicate that there has been a release of U(VI) during the last 0.8 Ma. Using the actual stoichiometric relationships as determined from the mineralogical and analytical studies of the orebody phases, Bruno and Duro (op. cit.) constructed a simple thermodynamic equilibrium model of the major co-existing mineral phase stability fields (Fig. 2.3). From this they could show that progressing from the stability domain, where unaltered $UO_{2.23}$ co-exists with PbO (as solid solution in this phase) and Fe(II) minerals, pyrite and siderite, to the altered $UO_{2.16}$, implies a release of U(VI) as oxidant. This would result in the oxidation of Fe(II) minerals to Fe(III) oxyhydroxides, i.e. a feasible mechanism to explain the red colouration in the clay adjacent to the massive ore/clay interface. The net result would be an overall decrease of the redox state of the orebody.

Coffinitisation implies a further depletion of both U(VI) and Pb(II) resulting in, on the basis of the actual measured oxygen fugacities in the orebody, the formation of sulphide minerals such as chalcopyrite and galena.

In summary, Bruno and Duro (op. cit.) propose that the Cigar Lake ore deposit has evolved from slightly oxidising to clearly reducing conditions from the period of ore formation to the present day. The Precambrian atmosphere is invoked to explain the initial slight oxidation of the Cigar Lake uraninites (UO_2 to $UO_{2.25}$) at the time of ore emplacement, which is actually observed in uraninites Type I at Cigar Lake. The hypothesis is

that the formed U(VI) was the active oxidant involved in the oxidation of Fe(II) to haematite and Fe-oxyhydroxides and, naturally, this would take place at the massive ore/clay interface. This phenomenon is consistent with present theories on ore formation (Sub-section 4.1) and by the very minor influence played by radiolysis reactions (Sub-section 3.1).
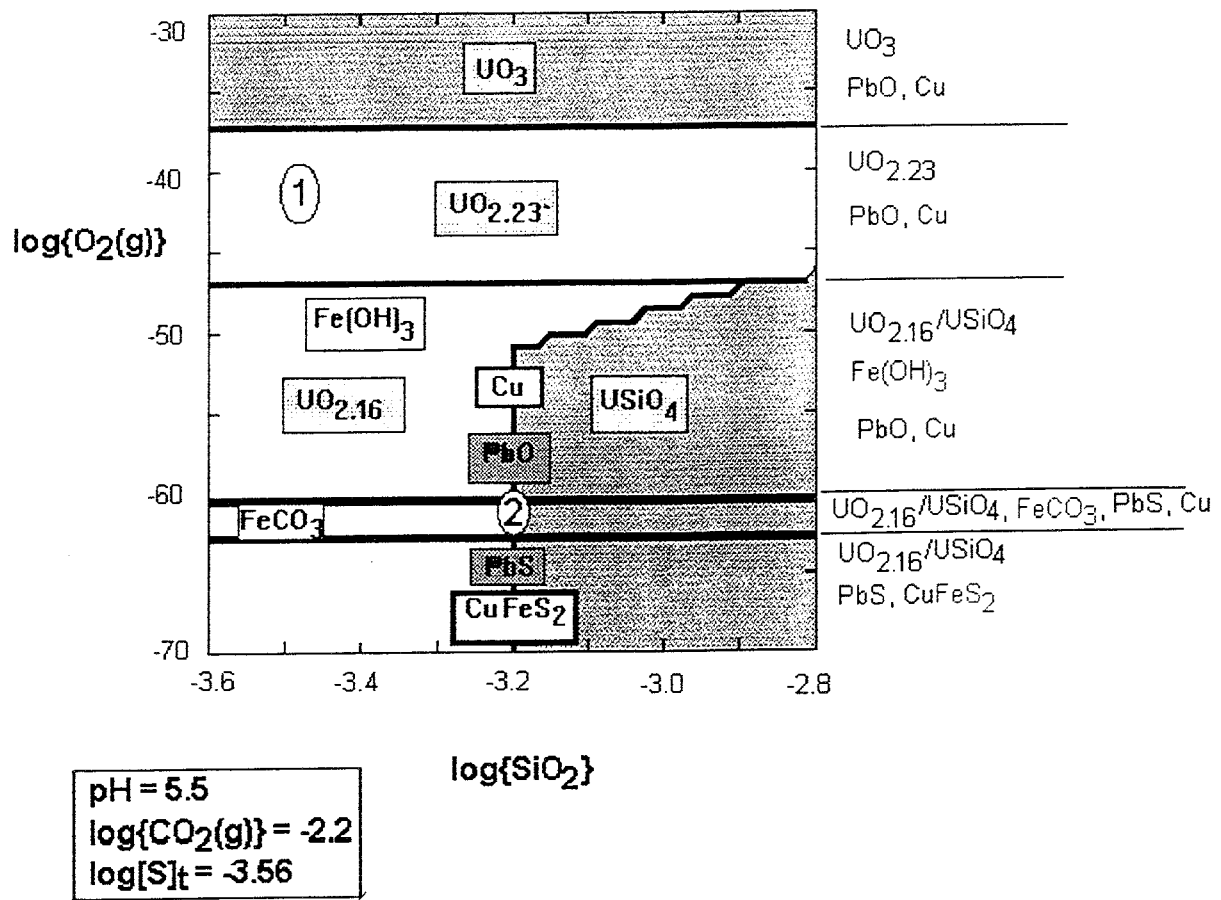

Figure 4.1: Stability phase diagram illustrating the major evolutionary steps participating in the ore formation process

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3. GEOCHEMISTRY OF THE GROUNDWATERS

3.1 TESTING OF KINETIC MASS TRANSFER MODELS

3.1.1 Introduction

Generally the groundwaters in and around the Cigar Lake uranium deposit are characterised by neutral to near-neutral pH (~6-8), by low TDS contents (~60-240 mg/L), by decreasing redox potentials towards the orebody (~+25 to -25 mV), and by the overall low U content (usually <30 μg/L) (Cramer and Smellie, 1994). Within the Upper Sandstone, and largely also in the Lower Sandstone, the groundwaters are HCO_3^- dominated with about equal levels of Na^+ ($+K^+$) and $Ca^{2+}(+Mg^{2+})$ among the cations combined with a low TDS content (<100 mg/L). In the vicinity of the basement, however, the water is Na^+-Cl^- in type with low alkalinity and a TDS content of 220-240 mg/L (Pettersson et al., 1992). The conceptual model for groundwater evolution at Cigar Lake (Cramer and Nesbitt, 1994a) is based on a simple downward percolation of water from surface recharge, through the overburden and into the Upper and later the Lower Sandstone Fomations, eventually entering the vicinity of the orebody through progressively altered and mineralised Upper and Lower Sandstone horizons.

Because of the uncomplicated mineralogy and geochemistry of the sandstone formations, groundwater evolution is mainly characterised by the interaction of the waters with the clay and iron minerals in the rock. Surface waters react with the clay and iron mineral phases in the overburden; this results in groundwaters entering the Upper Sandstone which are already equilibrated with the clay minerals and rich in dissolved iron. At increasing depth through the Upper Sandstones, precipitation of ferrihydrites occurs, usually demarcated by a limonite-rich zone extending to around 100 m. At greater depths the groundwaters encounter the so-called bleached and hydrothermally altered sandstones; subsequent reaction with Fe-sulphides (e.g. marcasite and pyrite) and siderite reduces the oxidation potential to well within the UO_2 stability field. These buffering reactions play a major role in preserving the stability of the uranium mineralisation.

The possibility of groundwater contributions from the underlying basement complex has been mentioned by Pettersson et al. (1992). Two features suggest otherwise: a) the hydraulics of the Cigar Lake groundwater system, and b) the increase in groundwater chlorinity as the orebody is approached may be related to leaching of salt residues (e.g. in fluid inclusions) from the hydrothermal systems which initially gave rise to the mineralisation (Cramer and Nesbitt, 1994a).

To achieve some further insight into the geochemical reactions characterising the evolution of the Cigar Lake hydrochemistry, Duro and Bruno (1995) have attempted to apply kinetic mass transfer models. As they point out, the equilibrium assumption is very useful to define the most probable geochemical evolution of a geochemical system, but its qualitative application has some limitations, even for waters with long residence times ($t_r > 10^4$ years). There is therefore the need to incorporate kinetics to predict the most probable evolution of groundwater conditions over the time-scales required for repository performance assessment which may extend from tens to hundreds of thousands of years.

3.1.2 Objectives and Methodology

To apply and test the kinetic mass transfer modelling approach at Cigar Lake, two main objectives were adopted relating to the massive clay/ore interface:

1. To test the present hydrogeochemical reaction model as proposed by Cramer and Nesbit (1994a), and

2. To test the observed mineralogical features.

To accomplish these tasks, various modelling approaches have been employed, for example, use of the:

* *NETPATH PROGRAM*: essentially used to interpret the net geochemical mass-balance reactions between an initial and final water along a determined groundwater flow-path direction,

* *STEADYQL CODE*: calculates the composition of the waters in the system at steady-state, and performs a sensitivity analysis on the influence of each of the parameters in the concentration of every component of the system, and

* *HARPHRQ CODE*: used to reproduce the evolution of pH and oxidation potential of waters along a determined groundwater flow-path direction.

One or a combination of these modelling approaches were used to study the stability of the following Cigar Lake geochemical systems: a) the Al-Si system, b) the U system, and c) the $Fe-CO_3-H_2O-S$ system. These were tested on specific conceptual groundwater flow pathways based on published hydrogeological (Winberg and Stevenson, 1994) and hydrogeochemical (Cramer and Nesbitt, 1994b) criteria. The following groundwater geochemical evolution pathways were chosen (Fig. 3.1):

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- groundwater flow above and adjacent to the massive clay/altered sandstone interface (borehole locations 211-67-81)

- recharging groundwater flow from the lower, weakly altered sandstone, down to the strongly altered sandstone above the massive clay/altered sandstone interface (borehole locations 71-67)

- potential upward groundwater flow from the basement to the mineralised sandstone just above the massive clay/sandstone interface (borehole locations 199-79-81)
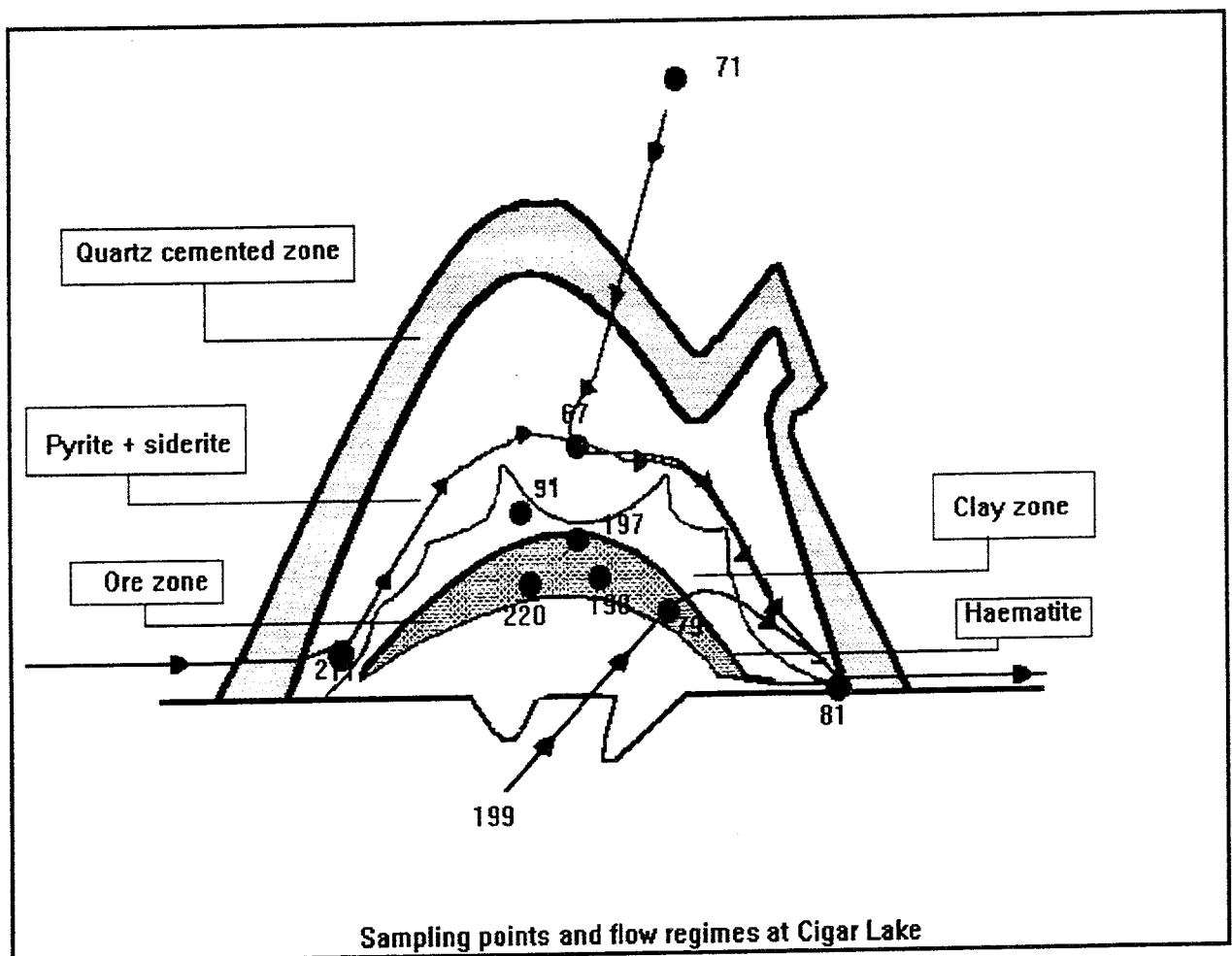

Sampling points and flow regimes at Cigar Lake

Figure 3.1:   Flowpaths used in the calculations

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3.1.3   Summary of Results

Al-Si System

The major aluminosilicates present at Cigar Lake are illite with
subordinate kaolinite, sudoite and traces of an illite-chlorite mixed layer
mineral (Percival et al., 1992). Based on prevailing hydrogeochemical
conditions, most sampled waters fall in the kaolinite stability field but are
not in equilibrium with this mineral (Cramer and Nesbitt, 1994a).
Assessment of the thermodynamic properties of the waters showed that all
are oversaturated with respect to illite and kaolinite (and also gibbsite
although this mineral has not been identified) and the results of Duro and
Bruno (1995) essentially confirm the findings of Cramer and Nesbitt (op.
cit.) and the predictions of Liu and Neretnieks (1994) in that the most
important processes influencing the passage of groundwater along the
selected hydraulic pathways are the dissolution of kaolinite and the
precipitation of illite (and gibbsite?); the subsequent conversion of illite to
kaolinite further explains the increased silica contents in these
groundwaters.

Duro and Bruno then modelled the same groundwater flow-paths based
on slow reaction kinetics for kaolinite dissolution and illite and gibbsite
precipitation. Groundwater flow velocities were based on hydraulic data
from Winberg and Stevenson (1994). The results showed close agreement
with the groundwater evolution flow-paths directions earlier derived from
studies at Cigar Lake.

U System

Analyses of groundwaters from the orebody indicate equilibrium with a
UO_{2+x} phase of stoichiometry and stability close to U_3O_7 (Bruno and
Casas, 1994). This is in good agreement with the mineralogical analysis
of uraninite from the orebody (Janeczek and Ewing, 1994).

Considering borehole 220 (orebody) as the starting point, Duro and Bruno
(1995), using a thermodynamic equilibrium approach, showed that as
higher oxidation potentials were approached at borehole locations outside
the orebody, the pH of the system decreases due to uranium being
released to the groundwater. During the calculation of this evolutionary
trend, the oxidation state of uranium oxide was always maintained within
the Eh-pH stability field for U_3O_7; no precipitation of any phase of
uranium exceeding U_3O_7 was allowed, thus conforming with the
mineralogical observations. As a result, these calculations reproduced
fairly well the experimental observations of Eh and pH in the U system.
This shows that the uranium system can be adequately explained by a
thermodynamic equilibrium approach; this is further supported by the fact
that long groundwater residence times (and therefore the possibility of
achieving equilibrium reaction values) have been calculated within the

orebody (Winberg and Stevenson, 1994).

Fe-CO₃-H₂O-S System

The Fe-CO$_3$-H$_2$O system was initially studied under equilibrium conditions and showed undersaturation for siderite and supersaturation for haematite, magnetite and goethite. The precursor for these highly crystalline Fe-oxides is the amorphous phase of Fe-oxyhydroxide. These findings support the earlier results of Cramer and Nesbitt (1994a).

Assuming dissolution of siderite and precipitation of Fe-oxyhydroxide, Duro and Bruno (op. cit.) introduced kinetic constraints to the site data to test part of the same groundwater evolutionary pathway used for the Al-Si system (i.e. boreholes 211-67). The simulation was successful in that it reproduced the iron concentrations found in solution in addition to the oxidation potential. No major change was observed in these parameters between boreholes 211 and 67; unfortunately few Fe^{2+} analyses exist from Cigar Lake to make more precise conclusions.

An important indication from these calculations is that it may be unnecessary to invoke an external oxidant supply (i.e. by water radiolysis as discussed in Section 4.1, and/or hydrothermal effects as discussed in Section 2.3) to explain the Fe(III) oxide concentrations present within the massive clay adjacent to the ore/clay interface. The formation of Fe(III) oxides may be simply explained by oxidation of Fe(II) phases such as siderite, as the Fe(II)/Fe(III) system appears to be in equilibrium in the Cigar Lake groundwaters.

The Fe-H$_2$O-S system was incorporated into the equilibrium redox calculations. This led to the conclusion that the geochemical processes involved in the evolution of the selected Cigar Lake groundwaters are, most probably, due to the appearance of Fe-sulphides, either as a result of the sulphurisation of the Fe-oxyhydroxides formed, or as a simple precipitation of these phases due to the presence of S in a reducing environment. This view is largely shared by Cramer and Nesbitt (1994a).

Comparison with the Al-Si system indicates that the evolutionary change in the Fe-H$_2$O-S system is much larger, indicating that a considerable input of sulphide is required. Thermodynamic equilibrium calculations show that Fe-S compounds are formed at the expense of pyrite (the only source of sulphide considered) and haematite dissolution. The Fe-S phase acts as a sink for sulphide; such monosulphides are known to coexist with pyrite reactions over long time periods. Assuming the formation of monosulphide, Duro and Bruno (op. cit.) added kinetic constraints to estimate: 1) the iron reduction phase, and 2) the formation of FeS. However, due to the complexity of the system, and the simultaneous presence of sulphate and sulphide, no clear conclusions could be reached. One implication is that the sulphate contents in the groundwaters are too

high to be explained by normal oxidative processes. This overestimation may be explained either by contamination during sampling, or, that another source of oxidants are available (e.g. by water radiolysis in the orebody; see Section 4.1).

3.1.4 Summary and Conclusions

A summary of the study and the main conclusions reached can be outlined as follows:

* Kinetic mass transfer models have been used with some success to enhance understanding of low temperature hydrogeochemical evolutionary trends at Cigar Lake.

* Combining equilibrium-based codes with kinetic mass transfer models is a promising approach to incorporate the time-dependence of slow water-rock reactions. For example, for waters with residence times over 10 000 years, the Al-Si system appears to be kinetically, rather than thermodynamically controlled.

* Modelling groundwater evolution of the Al-Si system has confirmed groundwater pathways based on hydrogeological criteria, in particular adjacent to the ore/clay interface. Some contributions may also come from downward percolation from the overlying lower sandstone horizons.

* The Al-Si system modelling also suggests some groundwater contribution to the orebody zone from the basement complex.

* It has been possible to explain the evolution of the redox $Fe(III(/Fe(II)$ system by assuming the oxidation of siderite to $Fe(III)$-oxyhydroxide. This is consistent with the mineralogy and may account for the formation of low temperature $Fe(III)$-oxyhydroxides within the massive clay adjacent to the ore/clay contact, without invoking additional sources of oxidants.

* The evolution of the U system may be explained by assuming equilibrium with uranium oxide phases of stoichiometry and stability close to U_3O_7.

* There is no clear geochemical explanation for the large amounts of sulphate in the orebody.

* The results from this study warrant consideration of reaction kinetics in repository performance assessment models, in order to predict the most probable geochemical evolution of the repository system over timescales of geological significance.

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4. NEAR-FIELD ISSUES

4.1 RADIOLYSIS: THEORETICAL CONSIDERATIONS AND FIELD EVIDENCE

4.1.1 Performance Assessment Implications

Radiolysis features as an important process in SKB's assessment of repository performance. Oxidants (e.g. OH-radicals, H_2O_2 and O_2 etc.) generated by radiolysis of water may change the redox conditions of the near-field of a repository. Hydrogen, the stable reductant, which is also generated from radiolysis, is not very reactive at ambient temperatures and is expected to migrate quickly out of the system. The net effect of radiolysis will therefore be one of oxidation. Such changes in the near-field chemistry may influence, in particular:

> * spent fuel stability; if oxidation of the UO_2 proceeds beyond U_3O_7 to U_3O_8, matrix release of trapped radionuclides may occur. A further release mechanism would be the oxidation and dissolution of U(IV) to U(VI).

> * radionuclide solubility; oxidation of U, Tc and Np to the more soluble uranyl, neptunyl and pertechnetate complexes.

> * buffering capacity; oxidation of Fe(II) to Fe(III), and sulphides to sulphates, will gradually reduce the buffering capacity of the near-field system, influencing both the solid and aqueous phases.

In all cases mobilisation and transport of radionuclides from the near- to the far-field may be enhanced, and this has important repository performance assessment implications. At Cigar Lake, the large amounts of high grade uranium ore presented the possibility of evaluating the potential influence of radiolysis (alpha, beta and gamma radiation effects) on uranium ore (UO_2) dissolution and the potential transport of radionuclides from the ore, through the surrounding clay halo and into the host sandstone formation.

4.1.2 Earlier Studies

In the context of Cigar Lake observations, general radiolysis model calculations (Christensen, 1994a) were carried out to:

> a) determine whether radiolysis products influence the oxidation and dissolution of UO_2 (uraninite), and

> b) determine the role of radiolysis in explaining the halo of

ferric iron oxide concentrations at the ore/clay interface.

The radiation dose rates used in these calculations were based on actual measurements on several uraninite (UO_2) phases from the Cigar Lake orebody. Calculations, assuming the simplistic concept of a UO_2 phase surrounded by water, predicted that mechanisms (a) and (b) were theoretically possible. Confirmation that these oxidative processes are occurring at Cigar Lake under present-day ambient temperatures would therefore provide strong evidence of water radiolysis.

Studies showed for case (a) some evidence that surface layers (only some microns in thickness) of uranium ore (UO_2) have been oxidised to higher mixed oxides (U_4O_9 to U_3O_7). This process, however, appears to be very limited as the threshold value of the corrosion potential, established by laboratory studies (Shoesmith and Sunder, 1992), may not have been exceeded. This subsequently led to a modification of the radiolytic model originally proposed to explain these oxidation phenomena (Christensen, 1990 a,b). As a result, it was shown that oxidation of UO_2 had been overestimated by an order of magnitude (Christensen et al., 1992). In fact, calculations using SKB's current performance assessment radiolysis models (using a threshold value subsequently found to be unreasonably low) predicted that the entire Cigar Lake orebody would have been totally oxidised within 18 to 170 Ma.

Karlsson et al. (1994) pointed out that the oxidation of U(IV) was not the only possible oxidant-consuming reaction in the ore zone. Oxidants, including those potentially resulting from radiolysis of water, can also react with components of the groundwater (e.g. Fe^{2+}, HS^-, DOC etc.) or diffuse out into the surrounding rock (e.g. O_2, H_2O_2) to react with mineral reductants such as siderite, uraninite and the various sulphide phases.

In case (b) model calculations confirmed that the radiolysis products of water can oxidise Fe^{2+} to the less soluble Fe^{3+}; this may account for the accumulation of ferric iron compounds surrounding the orebody marginal to the ore/clay interface. Whether small amounts of uranium have also accompanied the outward "redox front" movement of Fe^{3+} into the clay layer, forming co-precipitates with ferrihydrites, has not yet been established.

The presence of enhanced hydrogen contents in groundwaters sampled from the ore/clay zone was perhaps the most tangible evidence that supported radiolysis reactions occurring in association with the orebody.

The main conclusion to the Cigar Lake study relevant to repository performance assessment (Karlsson et al. (1994) was "that radiolytic oxidation in the near-field of exposed spent nuclear fuel, within the concept of an underground repository, cannot be ruled out. However, the net changes are considerably overestimated by models currently used for

performance assessment. The presence of some oxidation in the orebody indicates that the UO_2 in spent fuel will not necessarily consume all the oxidant generated."

Several questions still needed to be asked to explain the discrepancy between calculations and models based on experimental data, and the measurements and observations from the Cigar Lake orebody. The main area of uncertainty still revolved around the question of what has happened to the total oxidant production predicted by the radiolysis calculations. There is evidence of oxidation of UO_2 (uraninite), but this is very small; there is evidence that aqueous Fe^{2+} has been oxidised to Fe^{3+} which has subsequently precipitated to form $Fe(III)$ oxides, but this is orders of magnitude less than predicted; oxidation of sulphide to sulphate may also be linked to radiolysis, but again this would be inadequate. Hydrogen appears to have migrated out of the system, so why the disparity between observed and calculated effects of oxidation? Is the problem one involving basic theoretical misconceptions, inadequate experimental data, partial recombination of the radiolysis products (i.e. when H_2O_2, O_2 and residual H_2 revert back to water), or incomplete field data which have failed to reveal other oxidised mineral phases? These questions have been addressed in this reappraisal of the Cigar Lake Analogue Project.

4.1.3 Present Studies

Present studies set out to address some of the fundamental issues of radiolysis reactions and their potential influence on Cigar Lake observations. In particular:

1) A reappraisal of water radiolysis calculations,

2) Modelling the geometric radiation dose distributions from UO_2 grains, and

3) Comparison of observed radiolysis evidence from the Cigar Lake orebody with calculated predictions.

Supplementary Radiolysis Calculations

New dose rates for alpha, beta and gamma radiation, based on theoretical calculations, were provided by M. Jansson (written comm., 1994; also this article). Using these data Christensen (1994b) carried out radiolysis calculations using the same procedure as originally outlined in Christensen (1990a,b). The main assumptions made were:

* a constant concentration of Fe^{2+} was available $(9 \cdot 10^{-6}$ M$)$

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* precipitation of Fe^{3+} at some concentration
  above 10^{-6} M

* reactions with UO_2 were disregarded

In the presence of iron no recombination of H_2, O_2 and H_2O_2 would occur in the surrounding aqueous phase. In general, the main conclusions reached were that hydrogen and iron are produced in stoichiometric amounts by alpha radiolysis of water on the surface of UO_2 particles. The hydrogen produced at the surface probably diffuses out into a water layer irradiated by beta and gamma radiation without any major recombination effects, and Fe^{2+} precipitates as Fe^{3+}.

Compared with the earlier calculations (Christensen, 1990a,b), there is no qualitative difference in the overall predicted radiolysis reactions using the new radiation dose rates; this was not unexpected. The main issue of concern here is to quantify the localised radiation effects around the UO_2 particles, in particular the influence of alpha radiation. Attempts to accomplish this are outlined below.

Modelling of Geometrical Dose Distributions from UO_2 Grains

The geometry of the dose distributions emanating from UO_2 grains into a surrounding layer of water has been modelled. The main objective was to establish what fraction of the radiation reaches the surrounding aqueous phase to initiate the radiolysis reactions? These mechanisms have been addressed by Jansson et al. (1994) and Liu and Neretnieks (1994a,b).

It is important to bear in mind the different properties of the three types of radiation, i.e. alpha, beta and gamma, since both the origin and absorption of the three differ markedly. The models consider UO_2 grains of natural uranium composition, of different size dimensions, and surrounded by an absorber, i.e. a film of water. The models have been used to calculate the radiation dose absorbed in the water at various distances from the particle surface.

Theoretical Background

Radiation from a decaying nucleus can be either mononergetic (alpha and gamma), or distributed from zero to a maximum energy (beta). The reason for beta radiation not being monoenergetic is that the total energy is transferred to a beta particle and an antineutrino, such that the total energy is randomly shared.

When calculating the radiation energy absorption and the resulting chemical changes, two parameters require to be known for the different radiation types; the *LET* value (or function) and the *G*-value. The *LET* (Linear Energy Transfer) value is the energy absorption per unit path

length of the absorber and varies with the energy of the radiation and the electron density of the absorber. The *LET* value increases as the radiation energy decreases. The *G*-value is the radiation chemical yield in moles per unit absorbed energy.

Alpha and beta particles interact with matter by elastic or inelastic collisions with the electrons of the absorber. The major difference is that the alpha particle is much heavier and thus travels in a straight track and with a much lower velocity than a beta particle with the same energy. This means that an alpha particle has a much higher *LET* value than a beta particle with the same energy. With nearly the same weight as the orbital electrons the beta particle will travel a greater distance and change direction at almost every collision. Gamma radiation is absorbed principally by three mechanisms; the photoelectric effect, Compton scattering and pair production. Compton scattering is by far the dominating process; pair production only dominates at gamma energies higher than 10 MeV, i.e. gamma photons from radioactive decays do not lose energy by pair production. In the two former mechanisms the gamma photon loses its energy by interaction with the electrons of the absorber, producing secondary electrons which lose their energy in the same way as beta particles. The chemical effects are therefore comparable for beta and gamma radiation, although the *LET* value for gamma radiation increases more rapidly with decreasing energy than for beta radiation.

When modelling the dose rates or energy deposition in the surroundings of uranium-bearing minerals, the two decay chains of uranium have to be considered; ^{238}U and ^{235}U. Natural uranium constitutes 99.275% ^{238}U which has a half-life of $4.5 \cdot 10^9$ years, the remainder is ^{235}U with the half-life of $7.0 \cdot 10^8$ years. The ^{238}U decay chain consists of eight different alpha and six different beta decays, while ^{235}U has seven alpha and four beta decays. In each alpha (or beta) decay, the ejected particle can have from one up to eight different energies. The energy levels of the gamma radiation that carries the remaining nuclear energy are numerous. The two decay chains contain more than 1200 different energy levels with different relative occurrence.

Since alpha particles travel in straight tracks, rather simple geometrical models can be used as a basis for a global model. In the conceptual model for alpha radiation, UO_2 grains were taken to have a spherical (Jansson et al., 1994) or a cubic (Liu and Neretnieks, 1994 a) geometry. In both cases it is assumed that the UO_2 grain is larger than the trajectory of the alpha particle. The central region of the grains therefore represent areas from which no alpha particles will escape, and all kinetic energy of the alpha particle will be absorbed within the UO_2 grain. In the outer regions, some of the alpha particles will escape into the water layer at the grain's surface. The number escaping and their energy will depend on the distance from the surface and the angle of trajectory of the particle.
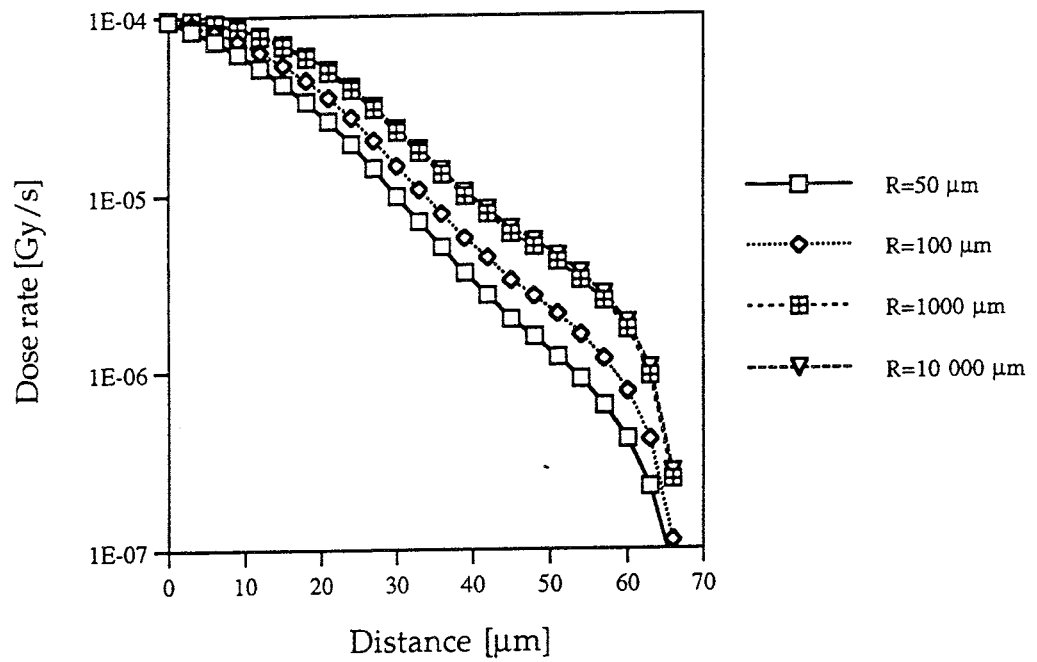
Figure 4.1:   Alpha dose rates at varying distances and radii (R) for an
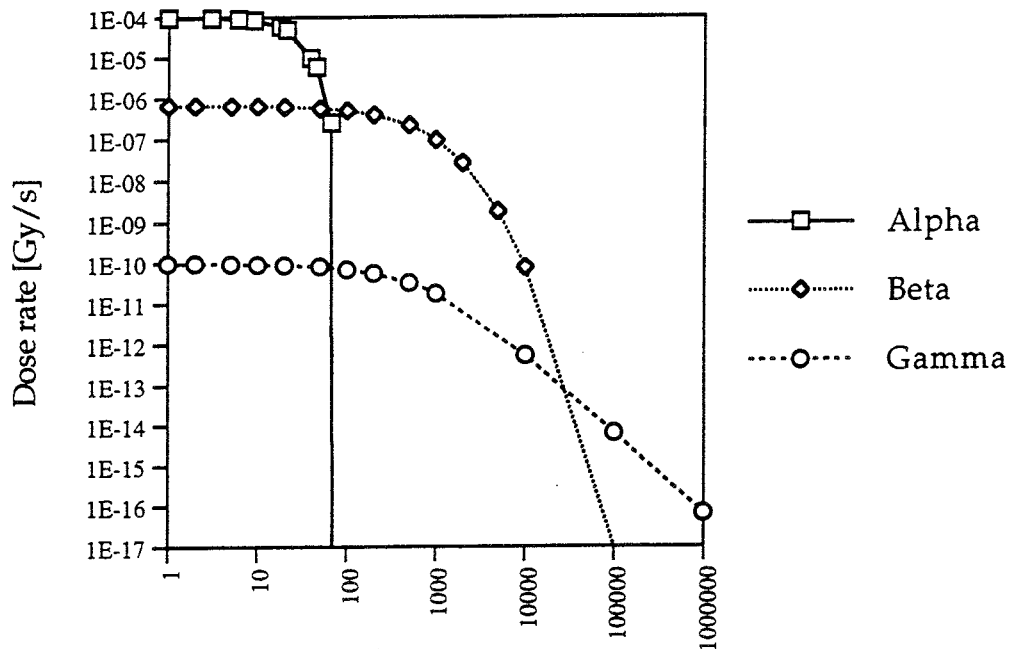   absorber with density 1 kg/dm³

Figure 4.2:   Beta and gamma dose rates at varying distances and radii (r)
                for an absorber with density 1 kg/dm³

For beta radiation, since two particles are ejected simultaneously (beta and antineutrino particles), the exact energy of a beta particle cannot be predicted, although the mean and the maximum energy is characteristic for the decay.

The nuclei formed after alpha- or beta-decays are often excited and gamma radiation is the result of relaxation of such nuclei. Since gamma photons have no mass or charge, gamma radiation has the longest range of the three radiation types.

In effect, for a UO_2 source the beta particles have a longer range of ionising radiation (millimetres) than alpha particles (microns), but less than gamma particles (centimetres). Of course this depends on the electron density of the absorber.

The Models

Based on the simple concept of a spherical UO_2 grain surrounded by water, Jansson et al. (1994) calculated, as a first step, the alpha, beta and gamma dose rates in water as a function of distance from the particle surface, for particles of different size ranges. For alpha radiation the surface dose rate dropped off rapidly over a distance of 65-70 µm from the particle surface, irrespective of the chosen grain sizes which ranged in radii from 50-10 000 µm (Fig. 4.1). Grains with a radius greater than 100 µm showed a constant alpha dose rate at the grain surface of $9.6 \cdot 10^{-5}$ Gy/s; this dose rate was used by Christensen (1994b). For beta and gamma radiation (Fig. 4.2), the dose rate drop off was more rapid for beta (within 100 000 µm from the grain surface) than for gamma (>1 000 000 µm from the grain surface).

The geometric dose distribution was then modelled for the three radiation types assuming a UO_2 grain of radius 1 mm. The calculated ratio between the maximum dose rates for the grain was found to be roughly $100:1:10^{-4}$ respectively. The fraction of the total radiation that escapes from UO_2 grains at different energies and grain diameters was also calculated. The ratio of radiation available to the absorbing material was shown to increase with energy and decrease drastically with increasing grain size.

As the alpha radiation dose rate close to the UO_2 grain is much higher than that of beta and gamma radiation, alpha radiation will thereby locally produce oxidants in greater concentrations than beta and gamma. Moreover, the hydrogen atoms, hydroxyl radicals and electrons formed from water radiolysis by beta and gamma radiation, will consume some of the molecular oxidants (H_2O_2 and O_2) produced from alpha radiation (Jansson, 1995).

In summary, the models of Jansson et al. (1994) and Jansson (1995) illustrate the following features important to radiolysis reactions:

* alpha radiation gives rise to high local dose rates in water close to the surface (within 70 µm) of a UO_2 grain; the major radiolysis reactions will occur in this region,

* for alpha radiation, the dose rate at the surface of the UO_2 grain is constant for grains of radii greater than 100 µm,

* for grain sizes smaller than 100 µm, the greater the radius the greater the surface alpha radiation dose rate and the greater the potential for radiolysis reactions to occur,

* the ratio of escaping alpha energy to the total energy increases with decreasing UO_2 grain size (Fig. 4.3), i.e. given an equal weight of large and small UO_2 grains, the potential for radiolysis reactions to occur at the grain surface will be greater for the smaller grain sizes, and

* beta and gamma radiation play a very minor role in radiolysis reactions compared to alpha radiation, however, they probably reduce the amounts of formed molecular oxidants resulting from water radiolysis.
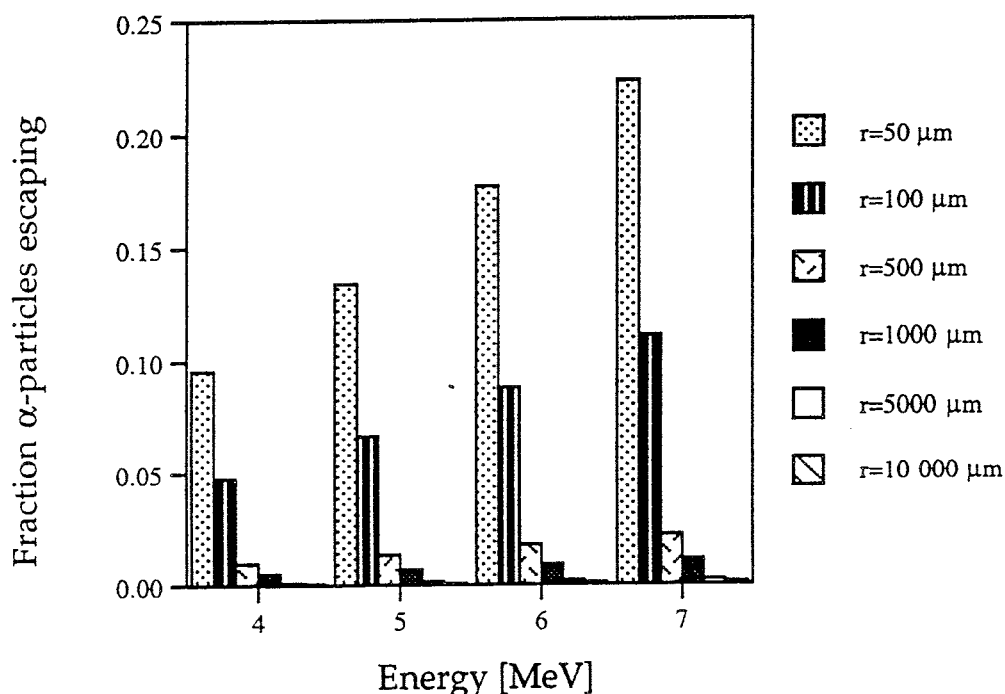

Figure 4.3: Fraction of the total activity that escapes the UO_2-sphere at different energies and sphere diameters.

In their approach, Liu and Neretnieks (1994a,b) assume a cubic uranium (UO_2) grain of specific edge length, of greater size dimension than the average trajectory of an alpha particle, and surrounded by a water film of constant thickness; alpha particles are emitted uniformly from everywhere within the grain. The central region of the uraninite grain, in common with the model of Jansson et al. (1994), represents the area from which no alpha particles will escape, and were all kinetic energy of the alpha particles will be absorbed within the grain.

The alpha emission points and the emission directions of the alpha particles were all randomly generated using the Monte Carlo Method. When these parameters are selected, and assuming that in all cases the energy is not fully dissipated, it is possible to calculate: a) the distance the alpha particle travels within the uraninite grain, and b) the distance it travels in the water film.

Using ore porosities ranging from 0.05 to 0.20 (based on estimations from the Cigar Lake orebody), the water film thickness surrounding the uraninite grain was calculated for each porosity. Then, for each film thickness, and assuming a constant linear energy transfer (*LET*), the fraction of total alpha radiation escaping and becoming available for radiolysis in the surrounding water film was calculated; this was found to range from 0.49 to 2.34% respectively.

Because beta and gamma radiation particles can travel greater distances than the size of the uraninite grain (plus water film) conceptualised in this model, several solid grains with their respective water films (referred to as "blocks") were considered. Using average trajectory values of beta and gamma radiation particles in a uraninite grain (1 mm and 5 cm respectively) and in water (10 mm and 20 cm respectively), and at ore porosities from 0.05 to 0.20, the ratios of the beta and gamma radiation energies available for absorption at the grain surface, over the total beta and gamma energies, were calculated and found to range from 0.52 to 2.44% at constant *LET*.

In summary, the model of Liu and Neretnieks shows that both the fraction of total alpha radiation escaping from the UO_2 grain and becoming available for radiolysis, and the fraction of this radiation energy deposited in the surrounding absorber (in this case the water film), is very small.

Model Comparison

To calculate the geometrical dose distributions from beta and gamma radiation, Jansson et al. (1994) have used theoretical models, orginally developed by radiophysicists for dose distributions in human tissue during radiotherapy. This enabled calculations of local dose rates. The radiolysis model of Liu and Neretnieks (1994a,b), in contrast, is a generic model developed for natural systems containing uranium mineral phases; the

Cigar Lake orebody is used as an example. Consequently, Liu and Neretnieks have distributed the beta and gamma energy equally over the whole Cigar Lake orebody, assuming a constant *LET* value, independent of energy and the electron density of the absorber, to obtain an average energy deposition in the water surrounding the UO_2 grains.

For alpha, beta and gamma radiation Jansson et al. have used the absolute activity per unit volume to calculate maximum dose rates, while Liu and Neretnieks first calculated the energy deposited in the water surrounding the UO_2 grains and then made a rough estimation of the oxidant production based on G-values for water.

When modelling alpha radiation Liu and Neretnieks used the Monte Carlo method to generate disintegration points of alpha radiation within the UO_2 grain, and to select the direction of the emitted alpha particle. Jansson et al. have based their model on alpha activity per unit volume, assuming that the emitted alpha particles will travel in all directions. The results are essentially identical, which can be expected for a uniform distribution of decay sites in the grains.

In both modelling approaches no consideration was given to the potential radiation shielding effects of matrix minerals in contact with the UO_2 such as clay phases and even other UO_2 grains.

The Cigar Lake Uranium Deposit: Testing of Models

Given the theoretical basis to the models, the next step is to test the models against actual observations and measurements from the Cigar Lake uranium orebody, although as pointed out above, the basic model of Liu and Neretnieks also includes data derived from Cigar Lake observations. From the outset the Cigar Lake uranium deposit exhibited certain disadvantages; for example, the general heterogeneous nature of the orebody itself and, on a smaller scale, the wide variation of uraninite grain sizes, their irregular distribution within the clay matrix and their tendency to occur as aggregates. Furthermore, because the orebody in reality should be considered a massive clay containing large aggregates and disseminations of uranium ore, the amount of circulating water in contact with the ore will be extremely small and localised. If there is any significant water movement at all, it is probably via a few discrete fracture/fissure systems. By far the greatest percentage of ore will be in direct contact with the dense clay matrix. This need not preclude the presence of water; the clay has a porosity and may be saturated such that films of water may be present at some ore/clay interfaces. However, the extent that this may be the case is at best speculative given existing petrographical data.

To overcome the variability and distribution of uraninite grain sizes, both Jansson et al. (1994) and Liu and Neretnieks (1994a,b) have employed

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the log-normal size distribution approach. The former chose two extremes from the Cigar Lake literature; between 1 μm and 1 mm, and from 100 μm to 1.5 cm, and the latter chose grain sizes from 5 to 1000 μm. Both groups allocated a density of 2.6 kg/dm^3 or 2615 kg m^{-3} for the surrounding clay matrix, which includes uraninite grains.

Assuming a uniform distribution of uraninite grains in the clay, Jansson et al. calculated for the 1 μm to 1 mm particle distribution an average distance between the grains of approximately 570 μm; for the 100 μm to 1.5 cm distribution the distance would be much larger as there would be fewer grains. This effectively means that alpha radiation determines the dose rate in the vicinity of the UO$_2$ grains, and since there is no overlap between the alpha fields, the beta radiation lies at a distance where the contribution of gamma radiation to the total dose can be safely neglected. They calculated that in the clay matrix the range of alpha, beta and gamma would be about 40% of that calculated for water. The minimum average dose rate for the Cigar Lake orebody would be in the order of 10^{-13} to 10^{-12} Gy/s. Considering these UO$_2$ size ranges, the main points illustrated by Jansson et al. are:

* The local dose rates of alpha radiation are much higher than those of beta and gamma radiation. At the surface of a UO$_2$ grain with a radius larger than 100 μm, the dose rate was found to be constant and equal to 9.6·10^{-5} Gy/s.

* The dose rate is expected to vary drastically within the Cigar Lake orebody. In the vicinity of the UO$_2$ grains alpha radiation dominates. Since alpha particles have a short range, this dominance ends sharply 20-30 μm from the grain. Beta radiation dominates outside the range of the alpha particle, but with a dose rate 100 times lower than in the alpha dominated region.

* The size distribution of the UO$_2$ grains is a very important factor since the fraction of the alpha energy escaping the grain depends on the grain size. Since great variation in the particle size distributions is given in the literature on Cigar Lake, two extreme cases were investigated. These showed that there is no overlap between the alpha fields and the maximum dose rate will therefore be the dose rate at the surface of a UO$_2$ grain (9.6·10^{-5} Gy/s).

* The molecular oxidant production (O$_2$ and H$_2$O$_2$) arises mainly from alpha radiolysis of water. Since the fraction of the escaping alpha energy is small and locally distributed, the production rate is also expected to be low.

When studying the application of alpha radiation to the Cigar Lake

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uranium occurrence, Jansson (1995) considered two factors to be crucial in theoretically estimating the oxidant production by water radiolysis: a) the UO_2 grain-size distribution, and b) the water distribution. As described above, the grain size determines the fraction of the total alpha energy that will escape from a UO_2 grain; the smaller the grain the larger the fraction of alpha energy escaping the grain and possibly depositing its energy in the surrounding water. To address point (b), if the UO_2 grains are surrounded by water, all escaping alpha particles will result in water radiolysis.

Jansson (1995) has clearly shown that the Cigar Lake grain-size distribution is an important factor; for example, the calculated relative ratios of energy escaping the UO_2 grains ranged from 3.52% (smallest size range; 1-1000 μm) to 0.067% (largest size range; 50-50 000 μm). Unfortunately, there are insufficient petrographic data from Cigar Lake to quantify the large-scale distribution of grain sizes.

The water distribution is another unknown factor in the Cigar Lake orebody, both in the massive ore itself and in the surrounding clay matrix. Recent studies by Karnland et al. (1994; this report) indicate that the clay beneath the orebody may have a porosity of >35%; these values are, however, questionable since the clay swelled before the sample was analysed (O. Karnland, per. commun., 1995). If it is assumed that such a high porosity is representative for the clay, then water would probably be in contact with all the UO_2 grains such that most of the alpha radiation would reach the water and cause radiolysis. This is considered unlikely. It is probably more realistic to consider that clay phases are in contact with some of the UO_2 surfaces, such that the escaping alpha energy would be absorbed by the clay in these cases. Moreover, the water that is bound to the clay is unlikely to produce large amounts of molecular oxidants since the OH· radical would probably attack the clay itself.

Jansson (1995) related the influence of clay porosity on the range of alpha radiation. Assuming that the total alpha energy escaping from the UO_2 grains is not influenced by the porosity, then the radiation energy absorbed by the water would be directly proportional to the porosity. However, as the electron density of clay is higher than for water, then the radiation range in clay should be shorter than that calculated for water and therefore dependent on the porosity. Jansson showed that by assuming that water is distributed homogeneously in the clay by amounts corresponding to the porosity, the total energy deposition of escaping alpha radiation in the water will be linearly correlated to the density of the clay and the porosity. Using a porosity of 10%, Jansson calculated that only 3.8% of the alpha radiation would be absorbed by the water; the rest would be absorbed by the clay phases.

In general, Jansson et al. (1994) and Jansson (1995) did not consider it appropriate to calculate a total average dose rate for the orebody because

of the uncertainty of the boundary conditions existing at Cigar Lake.

The radiolysis model of Cigar Lake presented by Liu and Neretnieks (1994a,b) is based on uranium grains of lognormal size distribution (5-1 000 µm) situated randomly, but sparsely, in a clay matrix and surrounded by water films of equal thickness (10 µm) (Fig. 4.4); the water thickness is directly related to the pore water being evenly distributed around all the grains, and using an average measured porosity of 10% from the Cigar Lake orebody. Of main interest is knowing the radiation source (i.e. the uraninite grains), calculating the portion of radiation energy absorbed by the water films, and thereby calculating the maximum possible oxidant production from the orebody.

It is assumed that the UO_2 grain (uraninite) is cubic and that the alpha radiation dose energy escaping from near the surface of the uraninite grain will be absorbed by the water film; any residual energy will be completely dissipated by an adjoining solid phase, either another uraninite grain or the clay matrix. The geometric dispersion of the ore constituents are less important for beta and gamma radiation as the respective emitted particle or photon will probably traverse several grain/water boundaries in the clay matrix. The total nuclear radiation energy from the uranium decay series was calculated by assuming secular equilibrium of decay.

The grain sizes, the alpha emission points and the emission directions of the alpha particles were all randomly generated using the Monte Carlo Method. For alpha radiation, two cases were considered.

Case 1: All alpha particles were assumed to have the same kinetic energy (5 MeV) and a similar range of particle penetration, i.e. 10 µm in uraninite and 40 µm in water. Furthermore, the linear transfer energy (*LET*) was assumed constant.

Case 2: All alpha particles were assumed not to have the same kinetic energy and *LET* was not assumed constant.

The calculated alpha particle ranges correspond closely to those assumed for Case 1: 10 µm for UO_2 and 40 µm for H_2O. The fraction of total energy absorbed by the pore water was calculated for every randomly selected alpha emission in every uraninite grain with a randomly selected grain size. The fraction was initially averaged for a single grain and then averaged for all grain sizes using the grain volume as a weighting factor. The calculations, based on an average porosity of 10%, gave a fraction of 0.0184 (Case 1) and 0.0197 (Case 2); assuming a constant *LET* and a variable *LET* therefore showed very little difference.
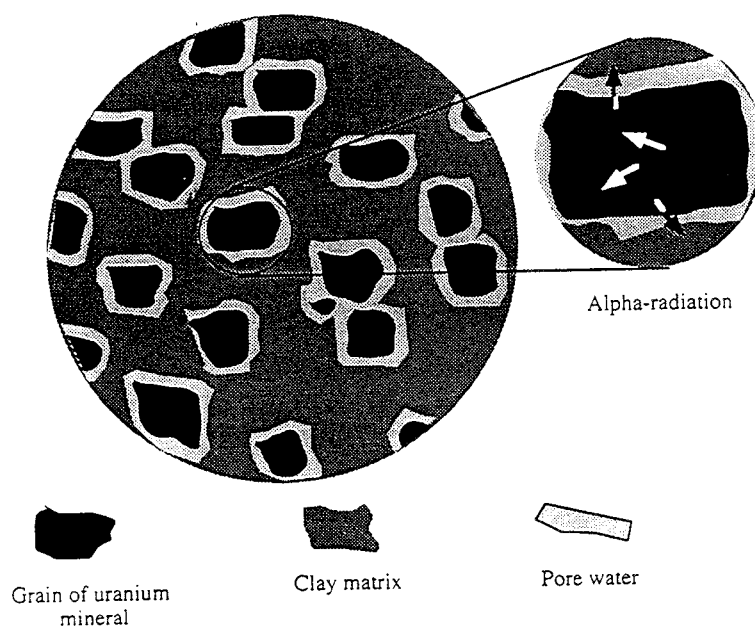
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Figure 4.4:   Schematic representation of the radiolysis model.

As discussed above, the interaction of beta and gamma radiation with absorbing media are much more complex to model. Compared to alpha particles, the interaction of beta and gamma radiation ranges over much longer distances (typically millimetres to centimetres), usually traversing many grains and water films. As such, their effect on the water film surrounding a single uraninite grain is very small in relation to alpha radiation. However, by considering a portion of the orebody as a dispersed porous medium, thereby minimising the importance of the geometric dispersion of the orebody constituents within this portion, the fraction of the total beta and gamma radiation energy absorbed by the surrounding clay pore water was calculated from the absorbed dose rate. Taking the average uranium content of the orebody to be 12% (based solely on uraninite) and the porosity to be 10%, the fraction of total beta and gamma radiation energy absorbed by the surrounding pore water was calculated to be 0.0436. This was also in reasonable agreement with calculations assuming a constant mass stopping power (0.0380).

In effect, the calculations showed that for an ore porosity of 10%, only about 1.0 - 2.0% of the total alpha radiation energy and about 2.0-4.3% of the beta and gamma radiation energy are available for deposition in the surrounding water film.

Liu and Neretnieks went on to calculate the total radiation energy per cubic metre of ore in the Cigar Lake deposit, assuming once again very large grains of uranium minerals, an average ore content of 12% by weight uranium, and a density of 2 615 kgm^{-3}. It was also assumed that

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beta and gamma radiation contribute in equal amounts. Using these energies the alpha, beta and gamma radiation energies (per second per m^3 of uranium ore) available for radiolysis at different porosities were also calculated. At porosities from 0.05 to 0.20 the alpha energies ($\cdot 10^4 Js^{-1}m^{-3}$) ranged from 1.42 to 6.74 respectively, and the beta and gamma energies ranged from 3.06 to 14.0 respectively. The total production rate of oxidant (i.e. water radiolysis) by alpha, beta and gamma radiation for the same porosities was calculated to range from 54.0 to $253.2 \cdot 10^{-12}$ eqv $s^{-1}m^{-3}$ of ore by using generally accepted G-values. Using a constant or variable *LET* made minimal difference to the outcome of these calculations.

Liu and Neretnieks (1994c) and Liu et al. (1994) have attempted to relate these calculations to present-day oxidant release predicted from the Cigar Lake deposit. If an orebody of grade 12% uranium and 10% porosity is considered, then, based on the above calculations, the maximum total oxidant production rate by water radiolysis is calculated at $114 \cdot 10^{-12}$ to $225 \cdot 10^{-12}$ eqv s^{-1} m^{-3} of ore. When this is compared with the predicted oxidant release rate of about $2 \cdot 10^{-12}$ eqv $s^{-1}m^{-3}$ of ore, a significant disparity is apparent. The reasons for this discrepancy may be several fold:

1) Overestimation of calculated oxidant production rate,

2) Underestimated present-day oxidant release,

3) The presence of other oxidant consuming components, and

4) Recombination of oxidants and hydrogen.

Overestimation of Calculated Oxidant Production Rate

The model calculations of Liu and Neretnieks (1994a,b) assume the Cigar Lake orebody to comprise uraninite (UO_2) grains of size range varying from a few millimetres to less than 1 μm (nominated size range used is 5-1000 μm); an average grain size of 100 μm has been quoted. These grains are embedded in clay; the clay and the grains together constitute the orebody. Micropores are considered to be always present in the orebody, and the apertures of these micropores are considered to be less than 30 μm. It is also assumed that these grains are accessible to water via the micropores such that they are surrounded by a water film of thickness 10 μm; the micropore apertures are considered to be at least twice the water film thickness, i.e. 20 μm. In the calculations the orebody is considered to comprise 12% uranium and has been allocated a porosity of 10%.

Because of the enormous size, complexity and heterogeneous nature of the Cigar Lake deposit, there are insufficient petrographic data available to obtain an accurate representation of all the mineralogical textures and

microstructures. As a result, estimations and basic assumptions have to be made. On balance, most of the assumptions made by Liu and Neretnieks and Liu et al. reflect the extent of present knowledge at Cigar Lake. There is, however, one obvious exception, and that is whether all the uraninite grains are in contact with water. It might be an obvious fact that the clay, at 480 m below the water table, should be totally saturated with water, and thus the ore in contact with the clay will also have access to water. This is disputed, however, by Jan Cramer (written comm., 1994) who considers the clay undersaturated with respect to water, such that much of the 80% of ore embedded in the clay will not have access to water. Furthermore, SEM imaging has suggested that micropore apertures are nearer to 5 μm in width.

On this basis, if it is conservatively assumed that 80% of the uraninite grain boundaries have no access to water, and that the remaining 20% have, will this result in a marked reduction in the oxidant production rate? According to Liu (written comm., 1995) this would not be so; Liu states that if only 10% of the uranium grain boundaries are accessible to water, the numerical result of the calculations would only be scaled down by one order of magnitude.

Although Jansson et al. (1994) and Jansson (1995) have not calculated a total average oxidant release from the orebody, due to the uncertainty of important boundary conditions, they have shown the importance of grain size and extent of water distribution on oxidant production. For example, the greater the UO_2 grain size range chosen, the less the relative ratio of energy available for water radiolysis which would escape the UO_2 grain. A greater UO_2 grain size range than that chosen by Liu and Neretnieks (5-1000 μm) would therefore further decrease the amount of oxidant production. At the moment the choice of size range is rather arbitrary because of a general lack of quantitative petrographic data covering the Cigar Lake orebody.

Jansson also points out that it is unlikely that a water film exists around each UO_2 grain; it is more realistic that clay phases (or in some cases other UO_2 grains) are in close contact with at least part of the UO_2 grain surface, and along these contacts some of the water is bound to the clay. Assuming a clay matrix porosity of 10%, Jansson has calculated that only 3.8% of the alpha radiation will be absorbed by the water; the rest being absorbed by the clay phases.

Finally, if the average uranium content of the Cigar Lake orebody is assumed to be 7.9% (J. Cramer, written comm., 1994) and not 12% as chosen by Liu and Neretnieks, the predicted oxidant release rate would be reduced by 40%.

In conclusion, whilst the models of Liu and Neretnieks have used assumptions based on current data from Cigar Lake, the extensive size

and heterogeneity of the orebody, and the highly variable distribution of water within this orebody, prohibit important boundary conditions to be satisfactorily established. Jansson et al. and Jansson have underlined that to assume: a) a reduction in the total ore content of the orebody, b) an increase in UO_2 grain size range, and c) most of the water surrounding the UO_2 grains is bound in the clay, would lead to a reduction in the total average oxidant release for water radiolysis. However, whether this is still adequate to fully explain the disparity between calculated and predicted oxidation production still remains uncertain.

Underestimation of Present-day Oxidant Release

Present-day oxidant release from the Cigar Lake deposit due to water radiolysis reactions has been focus of considerable attention. Liu and Neretnieks (1994c) and Liu et al. (1994) have developed a near-field release model and tested it against known helium release from the Cigar Lake deposit. In accordance with field observations, the uranium release rate predicted by the model was calculated to be extremely low. Radionuclide in situ generation and decay were also studied by modelling the release of ^3H, ^{14}C and ^{36}Cl, and the measured concentration gradients of hydrogen were used to estimate the net rate of radiolysis. Evidence of oxidant production by radiolysis in the system was related to the presence of sulphates, formed by the oxidation of sulphides. Liu et al. also found good agreement between the estimated rate of formation of the reductant hydrogen, and the oxidising component found in the sulphate.

This conclusion has not been reached without some controversy. The problem concerns the elevated sulphate contents that have been obtained from borehole 220 located in the orebody, and which form part of the argument of Liu et al. Jan Cramer (written comm., 1995) confirms the collection of elevated contents of He and H_2 in groundwaters from within and immediately adjacent to the orebody in general, but considers the elevated sulphate contents in borehole 220 as an artefact to drilling activities which have resulted in oxidation of sulphide present in the fine drilling debris material; all subsequent sampling recorded sulphate levels not significantly higher than the surrounding sandstone host locations. This, however, could also be explained by the limited presence of high sulphate waters initially within the orebody (i.e. a relatively closed hydraulic system) which were quickly exhausted during the initial sampling campaign. Subsequently, continued pumping and sampling only served to dilute/replace any residual sulphate waters by more dilute external formational water.

The debate is continued by Jinsong Liu (written comm., 1995) who considers, from a statistical viewpoint, that as the He and H_2 contents are also high in this borehole sample, and H_2 production is a result of radiolysis, then high sulphate contents (i.e. from oxidation driven by radiolysis) should also be valid. Furthermore, Liu also suggests that the

rapid oxidation of sulphide to sulphate in the drilling debris, during the short timespan covering drilling and subsequent sampling, is not kinetically possible.

Regardless of the debate, however, the predicted oxidant release from the Cigar Lake deposit is small, and would be even less if the elevated sulphate contents were neglected. Therefore the apparent wide disparity between the total calculated oxidant production rate by radiolysis, and the predicted present-day release of oxidants, still remains to be explained.

The Presence of Other Oxidant Consuming Components

The presence of other oxidant consuming components, or sinks, may also contribute to the difference of two orders of magnitude between the oxidant release from the Cigar Lake orebody and the value predicted from the calculated energy deposition in water. Such oxidant sinks may include: a) oxidation of the UO_2 ore itself, b) oxidation of Fe^{2+} to form Fe(III) oxides, and c) oxidation leading to the breakdown of organic matter.

Below an attempt has been made to quantify the mass balance effects of such reactions on the Cigar Lake orebody, and to discuss the results in the light of observational evidence.

UO_2 ore oxidation

Earlier studies (Christensen, 1994a) showed some evidence of UO_2 ore oxidation to higher mixed oxides (U_4O_9 to U_3O_7), which may have been induced by radiolysis, but this was very limited. In addition, there is no evidence of reprecipitation of uranium that might indicate mobility of uranyl complexes. At face value these features suggest that water radiolysis was not a widespread phenomenon at Cigar Lake. However, recent laboratory studies on spent nuclear fuel (SKB FoU, 1995) showed that oxidants produced by water radiolysis apparently disappeared from the system leaving no detectable oxidation effects on the UO_2 spent fuel pellets. This hypothesis was later revised to suggest that the oxidants had probably been consumed by oxidation processes occurring within the spent fuel matrix, but at a level below detection. These results have important performance assessment implications, and once again the Cigar Lake analogy may be used as support to laboratory studies.

Taking the total oxidant production rate by water radiolysis calculated from Cigar Lake, since formation of the orebody, as being $1 \cdot 10^{-12}$ ekv s^{-1}m^{-3} of ore in 10^9 years (see above; Liu and Neretnieks, 1994c), this would result in the oxidation of 3.6 metric tonnes of U(VI) m^{-3} of the orebody if all oxidants were to react with the UO_2. This is far in excess of what is observed.

Oxidation of Fe^{2+}

There is evidence that water radiolysis reactions can lead to the oxidation of Fe^{2+} to form Fe(III) oxides (Christensen, 1994a). These reactions are supported by the presence of large amounts of precipitated $Fe(OH)_3$ within the massive clay adjacent to the ore/clay interface. Using the same premise as above, the amount of $Fe(OH)_3$ expected to be produced by oxidation from 1 m^3 ore would be around 3.2 metric tonnes. Although considerable amounts are observed at Cigar Lake, there is also evidence to suggest that much of the $Fe(OH)_3$ is of hydrothermal origin (see Chapter 3). This would, in common with U(VI) production, indicate that radiolytic production of $Fe(OH)_3$ is much less than this calculation suggests.

Breakdown of organic matter

Organic matter in the Cigar Lake orebody occurs mostly as graphitic pellets; the reconstituted graphite derives initially from the underlying basement graphitic pelites (3-10% carbon) which have played an important role in the hydrothermal formation of the orebody. In the presence of oxidants (e.g water radiolysis) this organic material may break down to carbon dioxide and water. Calculations show that during the life-span of the Cigar Lake orebody, some 240 kg of organic material, given the net formula CH_2O, would be removed from 1 m^3 of ore. There is no petrographic or geochemical evidence at present that would support such a removal.

Summary

The above reaction processes were considered to give an idea as to the magnitude and order of changes anticipated to result from water radiolysis of the Cigar Lake orebody. Based on the calculated rate of H_2 escape, an oxidant production rate of 10^{-12} ekv $s^{-1}m^{-3}$ (as compared to the maximum calculated rate of 114-$225 \cdot 10^{-12}$ and to $2 \cdot 10^{-12}$ as indicated by hydrogen release) over a period of 10^9 years (as compared to the life-span of the Cigar Lake deposit of $1.3 \cdot 10^9$ years) would yield either 3.4 metric tonnes of $Fe(OH)_3$ and/or consume 240 kg of organic material (CH_2O) and/or oxidise 3.8 metric tonnes of uranium [U(IV) to U(VI)] per m^3 of ore.

What is the evidence for these reaction processes having occurred? The problem with estimating Fe(III) production is that ancient hydrothermal processes, and potentially other water/rock interaction processes, have probably contributed to the observed Fe(III) oxide concentrations within the massive clay adjacent to the ore/clay interface. Consumation of organic material is difficult to estimate because of a lack of detailed petrographic and analytical data. Oxidation of U(IV) to U(VI) as observed from detailed studies is considerably less than calculated.

The only remaining sink for the primary oxidants is the oxidation of sulphide to sulphate which has been estimated to consume some 250 kg of pyrite 1 m^{-3} ore. In common with the other reaction processes, however, this is also in excess to that observed.

The main conclusion is that the oxidant production rate from water radiolysis should be at least one (and possibly two) orders of magnitude less to explain the discrepancy between the calculated and maximum values. Based on the above estimations, organic material should be reduced by one order of magnitude, iron by two orders of magnitude, and uranium by around three orders of magnitude.

Recombination of Oxidants and Reductants

Recombination has been suggested by Liu and Neretnieks (1994a,b) as a possible mechanism to remove the radiolysis oxidants from the system. This is based on work carried out by Christensen and Bjergbakke (1982) who suggested a back-reaction factor of the oxidants and reductants resulting in a 99% recombination such that only 1% of the oxidant and reductant produced was available for redox reactions. This closely conforms to Liu and Neretniek's calculated efficiency of radiolysis of about 1%, where the efficiency of radiolysis is defined as the actual oxidant production rate over the maximum possible oxidant production rate.

According to Christensen (1994b) the presence of iron in the system should prevent the recombination of H_2 and O_2. Unfortunately there are very few data relating to groundwater iron contents from the Cigar Lake orebody; those quoted range from <0.012-0.62 mg/L Fe(Tot) which may not be enough to prevent widespread recombination.

Another possibility recently discussed by Pedersen and Karlsson (1995) and emphasised in Section 5.4, is bacterial recombination of H_2 and O_2 during the formation of organic material, heat and water. Energy from radioactive decay may in fact be partly conserved as organic material in the form of bacteria.

There exist a number of genera and species of so-called "knallgas bacteria" which are able to consume the H_2 and O_2 products, actually using these products as a source of energy. Such bacteria may exist at Cigar Lake, and so an accumulation of organic matter would therefore be expected by this process. Estimations for 1 m^3 ore give around 240 kg (CH_2O); such concentrations, however, are not observed at Cigar Lake unless it is assumed that the organic matter was soluble and left the system, or, alternatively, was consumed in further microbial processes, for example, by iron- or sulphate-reducing bacteria.

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4.1.4 Summary and Performance Assessment Implications

Essentially the radiolysis studies at Cigar Lake reported here have helped to establish a much more theoretical basis to understanding the geometric radiation dose distributions resulting from single UO_2 grains of different sizes, and establishing what fraction of the radiation reaches the surrounding aqueous phase to initiate the radiolysis reactions. The results clearly show that alpha radiation gives rise to high dose rates in water close to the surface of a UO_2 grain (within 70 μm); in comparison beta and gamma radiation play a very minor role in radiolysis reactions, and may even reduce the amounts of formed molecular oxidants resulting from radiolysis. Assuming a UO_2 grain size of 1 mm, the calculated ratio between the maximum dose rates for alpha, beta and gamma was found to be $100:1:10^{-4}$.

Results from the modelling of single grains showed that the ratio of escaping alpha energy to the total energy increases with decreasing UO_2 grain size. Calculations have also shown that the larger the UO_2 grain the greater the surface alpha dose rate and therefore the greater potential for radiolysis to occur. However, given an equal weight of large and small UO_2 grains, the potential for radiolysis reactions to occur at the grain surface will be greater for smaller grains. Furthermore, the surface alpha dose rate is constant ($9.6 \cdot 10^{-5}$ Gy/s) for grains of radii greater than 100 μm.

The modelling results show that only a very small fraction of the total radiation energy from a UO_2 grain, irrespective of size, is deposited in the surrounding aqueous phase. If a porosity of 10% for the Cigar Lake orebody is assumed, only about 1.0-2.0% of the total alpha radiation energy and about 2.0-4.3% of the beta and gamma radiation energy are available for deposition in the surrounding aqueous phase. Molecular oxidant production (O_2 and H_2O_2) arises mainly from alpha radiolysis of the aqueous phase. Since the fraction of the escaping alpha energy is small and locally distributed, the production rate will also be expected to be low.

The maximum total oxidant production rate by water radiolysis for the Cigar Lake deposit has been calculated at $114 \cdot 10^{-12}$ to $225 \cdot 10^{-12}$ eqv s^{-1}m^{-3} of ore. These calculations are based on several assumptions from the Cigar Lake deposit which are arguably very conservative and may not always be scientifically sound, but they do reflect the present status of knowledge and are considered adequate for performance assessment purposes in that the production rates represent close to maximum values. A lack of field evidence, supported by a predicted oxidant release rate of only $2 \cdot 10^{-12}$ eqv s^{-1}m^{-3} of ore (even allowing for the elevated groundwater sulphate contents discussed above), show that the actual effect of radiolysis at Cigar Lake is significantly lower than the maximum possible rate. Where have these oxidants gone? It seems unlikely that large

amounts of radiolysis oxidant products have disappeared from the Cigar Lake orebody system without leaving some additional present-day traces. The earlier hypothesis that large accumulations of Fe(III) phases adjacent to the ore/clay interface might represent such traces, has since been discarded. However, small contributions of the less soluble Fe^{+3} to the groundwater system by water radiolysis is probably occurring and should not be ruled out.

The disparity between high calculated oxidant production rates and the low predicted oxidant release (supported by field evidence) had earlier been attributed to an overestimation of the net changes due to radiolysis by models currently used in performance assessment (Karlsson et al., 1994). However, despite the fact that this present study: 1) has used alternative radiation dose rates (based on theoretical calculations), 2) has developed a much greater theoretical understanding of the geometric dose distributions produced from UO_2 grains of size ranges present in the Cigar Lake deposit, 3) has considered the influence of other oxidant consuming components and reactions which might result in recombination of oxidants and hydrogen, and 4) has applied the latest field data to support basic mathematical assumptions in the models, an overestimation of radiolysis effects at Cigar Lake still appears to prevail. The most obvious reason for this is the uncertainty of important boundary conditions (e.g. water distribution and grain-size distribution) at Cigar Lake due to its complexity and heterogeneity, making calculation of average dose rates at the moment uncertain.

Despite the many remaining difficulties outlined above, however, advances have been made in testing and developing current radiolysis models used in SKB's performance assessment methodology. At Cigar Lake a model for radiolysis in a heterogeneous orebody material (UO_2 in clay) has been developed and tested. Although still on the conservative side, by overestimating the effects of radiolysis, the gap between calculated and predicted oxidant production has been narrowed significantly compared to earlier attempts.

4.2 THE EFFECT OF RADIOLYSIS ON THE STABILITY OF NATURAL URANINITE

4.2.1 Introduction

The development and application of alternative models that consider the potential radiolytic generation of oxidants in Cigar Lake have been discussed in Section 4.1. Recently within the SKB programme a ReDuctive Capacity (RDC) model has been developed to try to account for, on a macroscopic scale, observations from laboratory studies

regarding the effect of radiolysis in oxidant generation (Eriksen et al., 1995; Bruno et al., 1996). Furthermore, the validity of this model has been tested by application to long-term observations of uraninite stability in the Cigar Lake deposit (Bruno, 1995).

The chemical stability of spent fuel is very dependent on the evolution of pH and Eh; these in turn are dependent on the respective buffer capacities, i.e. alkalinity (acid neutralising capacity) and RDC, the reductive capacity (oxidising neutralising capacity). Knowing these two conditions makes it possible to describe the ability of the repository near-field to respond to external/internal chemical perturbations, for example the influence of radiolysis reactions.

As the RDC model is, in principle, a function of the concentration of generated radiolytic oxidants and therefore a function of time, it was used in the Cigar Lake context to study the dependence of the main parameters (e.g. estimated rates of oxidant generation and degree of uraninite oxidation) with time, thus deriving an overall expression for the rate of UO_2 (i.e. spent fuel analogy) matrix dissolution over geological timescales, in line with the expected lifespan of a repository system.

Experimental observations on UO_2 dissolution, i.e. unradiated UO_2, uraninite, Simfuel and spent nuclear fuel show that: 1) there may be some initial surface oxidation, for example due to storage time prior to deposition in the case of spent fuel, or, in the case of Cigar Lake uraninites, due to long-term geochemical effects in the geosphere, 2) there may be oxidant attack from radiolysis reactions and from the chemical interaction with groundwater, and 3) there may be the formation of secondary U(IV) and U(VI) alteration mineral phases; this will be dependent on the dissolved uranium content in the groundwater, on the surface area to volume ratio, on groundwater composition and on the velocity of the contact groundwater flow.

4.2.2   Testing of the Reductive Capacity (RDC) Model

4.2.2.1   Cigar Lake Uraninite Samples

The validity of the basic kinetic premises of the model has earlier been demonstrated by Casas et al. (1994) using natural uraninites from Cigar Lake. The RDC model was tested by exposing natural uraninite to air (P= 0.2 atm.) and maintaining an oxidant concentration of $2.31 \cdot 10^{-4} mol.L^{-1}$ (Bruno, 1995). The sample was subsequently characterised and no secondary uranium mineral formation was observed. However, the discovery of an initial oxidation layer described by Janeczeck and Ewing (1994) had to be taken into consideration; this was considered due to sampling and storage effects. The conditions considered, therefore, in testing the model, where in the first stage the sampling/storage oxidation effects and the dissolution of new UO_2 co-ordination sites (formed as a

consequence of dissolution of the oxidised surface layer), followed in the second stage by the dissolution of the UO_2 co-ordination sites.

The model calculations showed that the reductive capacity of experimental system was negative from the start and decreased with time. This was explained by the large continuous supply of oxidants to the system by air, in contrast to the small amount of uraninite sample used.

4.2.2.2   Cigar Lake Deposit

Although the situation at Cigar Lake is quite different from the experimental conditions just described, the results obtained gave sufficient confidence in the RDC model to apply it to *in situ* conditions.

4.2.3   Summary and conclusions

The modelled laboratory results are generally not dramatic; a rapid initial increase in oxidants is followed by steady state conditions, where the radiolytically generated oxidants are immediately neutralised by the UO_2 sites. This is believed to have resulted in a transition of pure UO_2 to slightly oxidised uraninite with a nominal stoichiometry of $UO_{2.33}$ (Bruno et al., 1996). This is supported by mineralogical observations, calculations of uranium concentrations in the ore zone (Bruno and Casas, 1994) and also through the application of kinetic transfer models to the Cigar Lake system (Duro and Bruno, 1995; Section 3.1, this report).

Attempts to establish the timescale for these initial oxidation processes in the Cigar Lake deposit, using air oxidation data on spent fuel as a function of time, suggested that it would take some 10^7 years at ambient temperatures to achieve complete oxidation of the orebody. Given that the ore was formed under hydrothermal conditions (around 200°C; Section 2.3, this report), a much shorter period after formation would be only necessary to convert the uraninite to $UO_{2.4}$. Since then, the Cigar Lake uranium ore has not undergone any major oxidation. This is in general agreement with mineralogical observations of present-day uraninite phases from the massive orebody (Janeczeck and Ewing, 1994).

As a general conclusion, despite some uncertainties in the Reductive Capacity (RDC) model, it is clear that the reductive capacity of the orebody became large and basically unchanged since the initial hydrothermal phase which produced the ore. The amount of radiolytically oxidant produced was balanced by the large reductive capacity of the uraninite content of the orebody. The modelled calculations suggest that there is no contradiction between the macro- and microscopic observations regarding the stability of the ore, and the modelling carried out regarding the radiolytic generation of oxidants.

4.3 PHYSICAL PROPERTIES OF AN ARGILLISED BASEMENT SAMPLE: COMPARISON WITH BENTONITE

4.3.1 Background

The majority of disposal concepts for the safe containment of high-level radioactive waste propose the use of bentonite clay as a packing material placed between the rock wall of the disposal hole and the metal canister which contains the waste. The main objective of the bentonite is to initially delay corrosion of the canister material by restricting groundwater contact from the surrounding bedrock; in the event of corrosion and canister penetration the bentonite will then serve to retard the mobility and dispersion of radionuclides to the geosphere. In the Swedish case the bentonite presently being considered is the so-called MX-80 type, a natural sodium bentonite (montmorillonite) from Wyoming, USA, which possesses suitable physical properties of hydraulic conductivity, swelling ability and rheological behaviour.

The properties of bentonite are determined by the interaction between water and the smectite component, usually montmorillonite. The mineralogical stability of the montmorillonite has been extensively studied in natural geological systems (e.g. natural analogues) and the most common alteration product is illite, a clay showing markedly inferior physical properties in the context of a repository buffer material. In this latter regard, however, proposed models of bentonite alteration during the lifespan of a repository system show sufficient montmorillonite stability over temperature ranges expected to occur under disposal conditions (i.e. <100°C). Of course repeated dehydration and extreme changes in pH, for example, may result in irreversible mineralogical conversion leading to illite. At total conversion to illite, the physical properties will be altered to an extent that depends on the character of the illite, both with respect to mineralogical composition and to microstructure. Oswald ripening, i.e. the growth of larger crystals at the expense of smaller, or other mineralogical processes, may lead to further time-dependent changes in the physical properties of the material (Karnland et al., 1994)

The Cigar Lake uranium occurrence, intimately associated with massive clays dominantly comprising illite, therefore offered the opportunity to study at first hand the role of illite (i.e. the worst case repository buffer scenario) in helping to shield the uranium orebody from water-rock interaction and eventual removal since its formation 1.3 Ga ago. Such information could provide valuable input data of buffer material properties to future repository performance assessments.

The general approach taken by Karnland et al. (op. cit.) was to characterise the Cigar Lake clay with respect to mineralogy and

microstructure, and to determine those physical properties important to repository performance assessment. These data were then compared with a MX-80 sodium bentonite and also a calcium bentonite (Moosburg) which is the clay buffer favoured by some disposal concepts.

4.3.2   Approach and Results

Clay samples were selected from one strategic drillcore, Bh 53 (see details in Percival et al., 1993), at one horizon in the altered basement complex some 10 metres below the massive ore/clay contact. The composition of the basement clays are, however, probably representative for the overall massive clay body as suggested by previous studies (see Percival, 1990 and Percival, 1994). The general physico-chemical properties of the basement sample were compared with a MX-80 sodium bentonite and referenced to other clay mineral examples taken from the literature (e.g. illite, muscovite, sudoite). More specifically the hydraulic conductivity, swelling pressure, angle of shearing resistance and cohesion were measured and compared with the MX-80 and Moosburg reference clay samples.

The analysed Cigar Lake clays, of measured bulk density 1.847 g/cm^3, typically fall within the general compositional range of illite to sudoite, and therefore do not surprisingly differ significantly from MX-80. The grain size distribution is non-typical for illite and sudoite; the major part of the material had a grain size greater than 50 µm, and less than 5% of the mass had a particle size within the clay fraction (<2 µm). This 5% may not be totally representative as large clay crystals (i.e. muscovite) may have been formed or small crystallites (i.e. illite and sudoite) may have been cemented into larger aggregates. Further study confirmed the clay fractions to be mainly muscovite/illite with subordinate sudoite, and measured ion-exchange capacities recorded 7.2 and 7.3 meq/100g, i.e. within the lower range of that expected for a mixture of illite and chlorite, and substantially lower than for illite. The larger clay grains tend to occur as branches (length 1-10 µm and width 0.1 µm) and show a general parallel orientation reminiscent of compaction textures; this differs from the smaller grain size fractions which tend to be characterised by more randomly oriented grains. Compaction is probably more a feature of the basement clays underlying rather than overlying the orebody.

A comparison of swelling pressures is illustrated in Figure 4.5, of hydraulic conductivities in Figure 4.6, and rheological properties in Figure 4.7. In all cases there is a marked difference between the behaviour of the Cigar Lake material and the MX-80 and Moosburg reference clays, the reference clays tending to indicate closely similar physical properties. The laboratory data underline the importance of ensuring high saturation densities in the clays to maintain the desired standard of physical properties for disposal purposes.
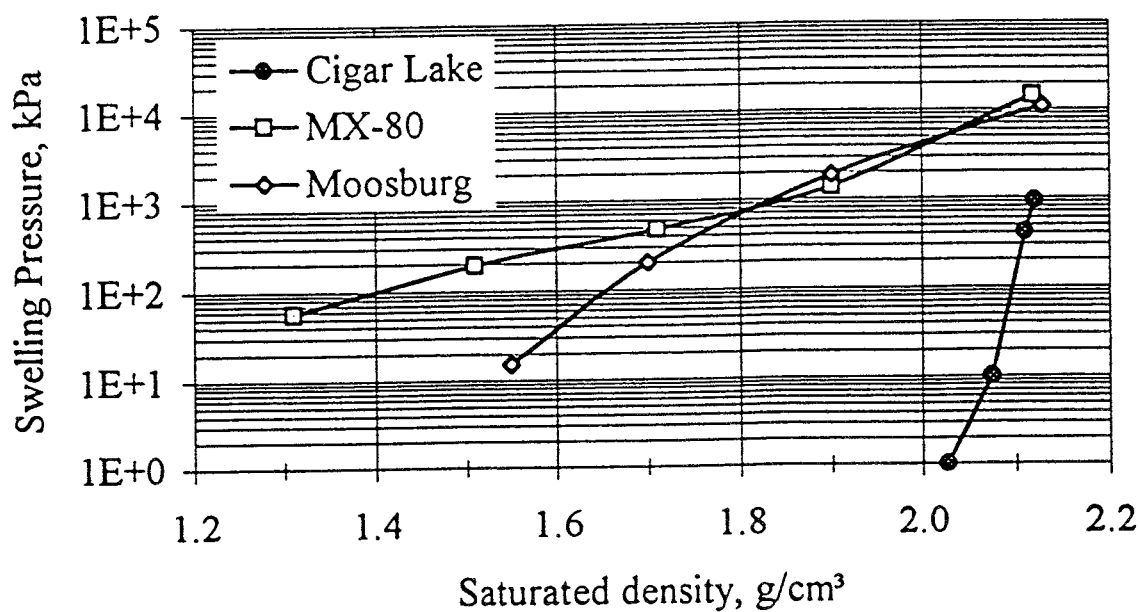
Figure 4.5: Swelling pressure of the Cigar Lake material and two commercial bentonites versus saturated clay density. MX-80 represents a natural sodium bentonite and Moosburg a natural calcium bentonite.
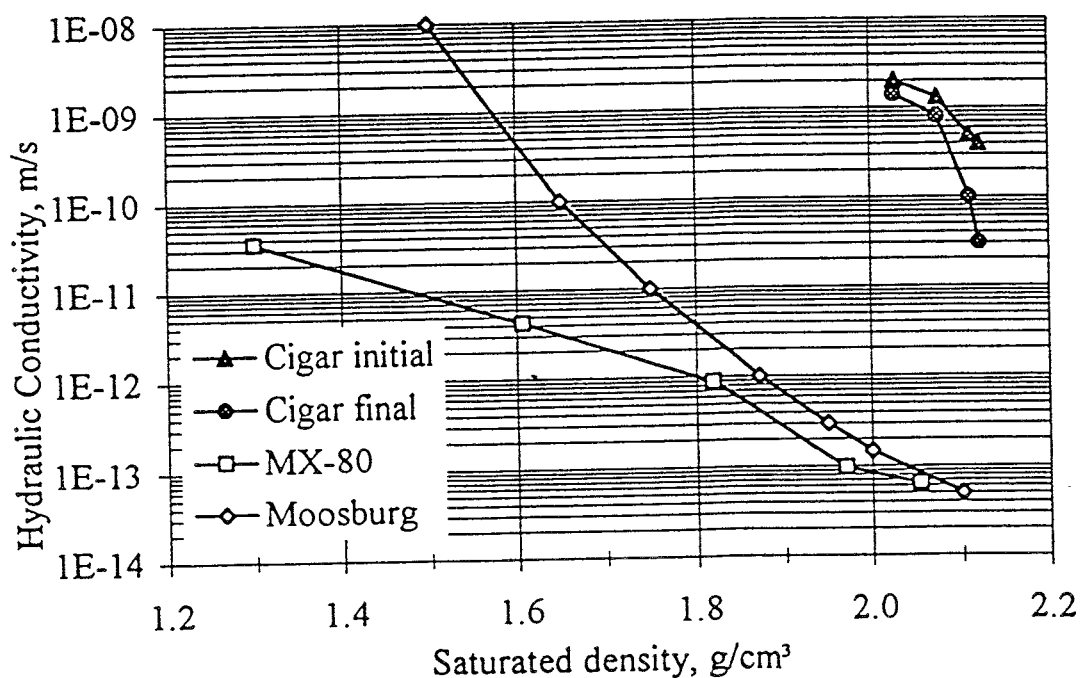

Figure 4.6: Hydraulic conductivity of the Cigar Lake material and two commercial bentonites versus clay density at saturation.
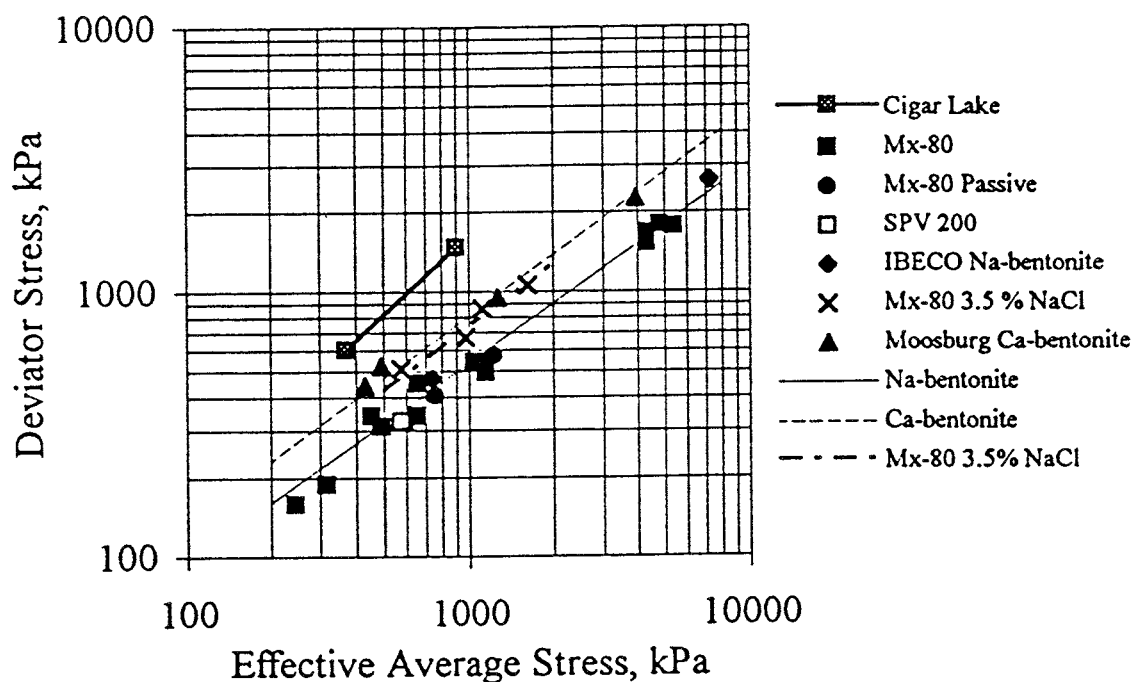
Figure 4.7:   Deviator stress at failure versus effective average stress for the Cigar Lake material (upper curve) and for several bentonite materials tested by different techniques and pore water solutions.

4.3.3   Conclusions and Performance Assessment (PA) Implications

Chemical and physical characterisation of the Cigar Lake core material shows the clay as representing a "worst possible repository case" of smectite to illite alteration with respect to crystal size, basal spacing and mineral-water interaction, although it should be pointed out that there is no mineralogical evidence at Cigar Lake that the original clay material was indeed smectite. Theoretical calculations by Shi (Chapter 2; Section 2.3), however, point to the formation of smectite and/or illite/smectite mixed layer phases during hydrothermal alteration of the host sandstones.

Assuming the conversion of smectite in the MX-80 reference clay to a clay form exemplified by the Cigar Lake material, changes in physical properties show:

* a decreased swelling pressure by at least one order of magnitude,

* an increased hydraulic conductivity by at least three orders of magnitude,

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* a loss of expandability and self-healing potential, and

* an increased stiffness and brittleness.

In the context of repository performance assessment, marked deterioration of bentonite would not only seriously threaten the integrity of the bentonite buffer itself, but ultimately the long-term stability of the canister and waste form. However several points should be considered at this juncture. Current PA buffer material alteration models show the unlikelihood that bentonite will undergo major alteration during repository timescales to the extent represented to-day at Cigar Lake. It should also be pointed out that for certain properties, direct comparison with the Cigar Lake clays can be misleading. For example, conversion of a smectite to an illite clay is normally accompanied by density changes. In a spent fuel disposition hole, such density changes do not occur since there is an established equilibrium existing between the water content in the clay and the confining over-pressure. This is not the case at Cigar Lake where there are no confining equilibrium conditions. In this case the water content in the clays will be expelled under excess overburden pressures, leading eventually to compaction. However, despite these reservations and the very poor buffer qualities measured from the Cigar Lake material, in practice, the massive clay (i.e. illite):

* has provided an effective, long-term sealing of the
   uranium orebody (i.e. during the 1.3 Ga since ore
   formation),

* is stable under suitable conditions over geological
   timescales, and

* is an efficient barrier to radionuclide and colloid
   migration.

Why the clay has functioned efficiently as a sealant may also be a function of thickness. In places the massive clay can be in exess of 10 metres, whilst at other locations the surrounding clay horizon may be non-existent. Unfortunately there exist insufficient data to presently address this issue. Of greater potential importance are the prevailing reducing groundwater conditions present over similarly long geological timescales; earlier studies at Cigar Lake have showed that very little uranium dissolution and radionuclide migration has occurred over the last 100 Ma.

In summary, studies at Cigar Lake have shown that the clays, whilst exhibiting inferior physical qualities to the bentonite types considered for repository disposal, have provided an efficient sealant to groundwater flow and also to radionuclide dissolution and migration over repository timescales. This is demonstrated by the: 1) large difference in hydraulic

conductivity (Winberg and Stevenson, 1994) between the surrounding permeable host sandstones (K= 5x10^{-6} m/s) and the hydrothermally formed clays (K= 1x10^{-9} m/s), and 2) the calculations and observations of radionuclide mass transport in the near-field of the orebody summarised by Liu et al. (1994). The chemical buffering capacity has been greatly facilitated by prevailing reducing groundwater conditions. Therefore, as long as the chemistry of the groundwaters is sufficiently reducing, a deterioration of the clay buffer material need not result in widespread radionuclide migration.

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5. FAR-FIELD ISSUES

5.1 HYDROGEOLOGY AND ITS COUPLING TO HYDROCHEMISTRY

5.1.1 Background

Based on hydrogeological criteria, groundwater flow in the Cigar Lake
area has been modelled at the regional and local scales by Winberg and
Stevenson (1994). The overall conceptual model has been further
constrained by the coupling of groundwater chemical and isotope
parameters (Cramer and Nesbitt, 1994). The hydrogeological conceptual
model for Cigar Lake is illustrated in Figure 5.1 and the major
conclusions, mainly taken from Cramer and Nesbitt (op. cit.), are listed
below:

* three distinct groundwater flow regimes characterise the area; local
(superficial Quaternary deposits), intermediate (Upper Sandstone) and
deep semi-regional (Lower Sandstone). Deep regional groundwater flow is
from south to north, and numerical modelling suggests that discharge
from all three regimes is towards Waterbury Lake,

* recharge to the intermediate regime occurs locally along fractures and
in places where the overburden is absent, whereas recharge to the semi-
regional regime occurs mainly to the south beyond the local scale of the
Cigar Lake deposit, probably at various points along deeply penetrating
fractures under local topographic highs. Semi-regional flow rates have
been estimated to be >10 ma^{-1},

* evolution of groundwater compositions, from recharge waters to
groundwaters characterising the clay and mineralised zones, involves
interaction with similar mineralogies in all three regimes; additional
leaching of interstitial salts also occurs. These salts are believed to be
relicts of ancient, diagenetic to hydrothermal saline fluids responsible for
ore formation and host rock alteration,

* the flux of the groundwater through the clay matrix hosting the uranium
mineralisation is very low, with etimated residence times for water in
contact with the ore of $>10^4$-10^5 a. Therefore diffusive, rather than
advective processes most likely control redox conditions within the
mineralisation.

To further test the general hydrogeological and hydrochemical
conclusions, a reappraisal of the hydrogeological understanding of the
Cigar Lake system was initially carried out, and different approaches were
then used to reexamine the hydrochemical evolution of the groundwaters
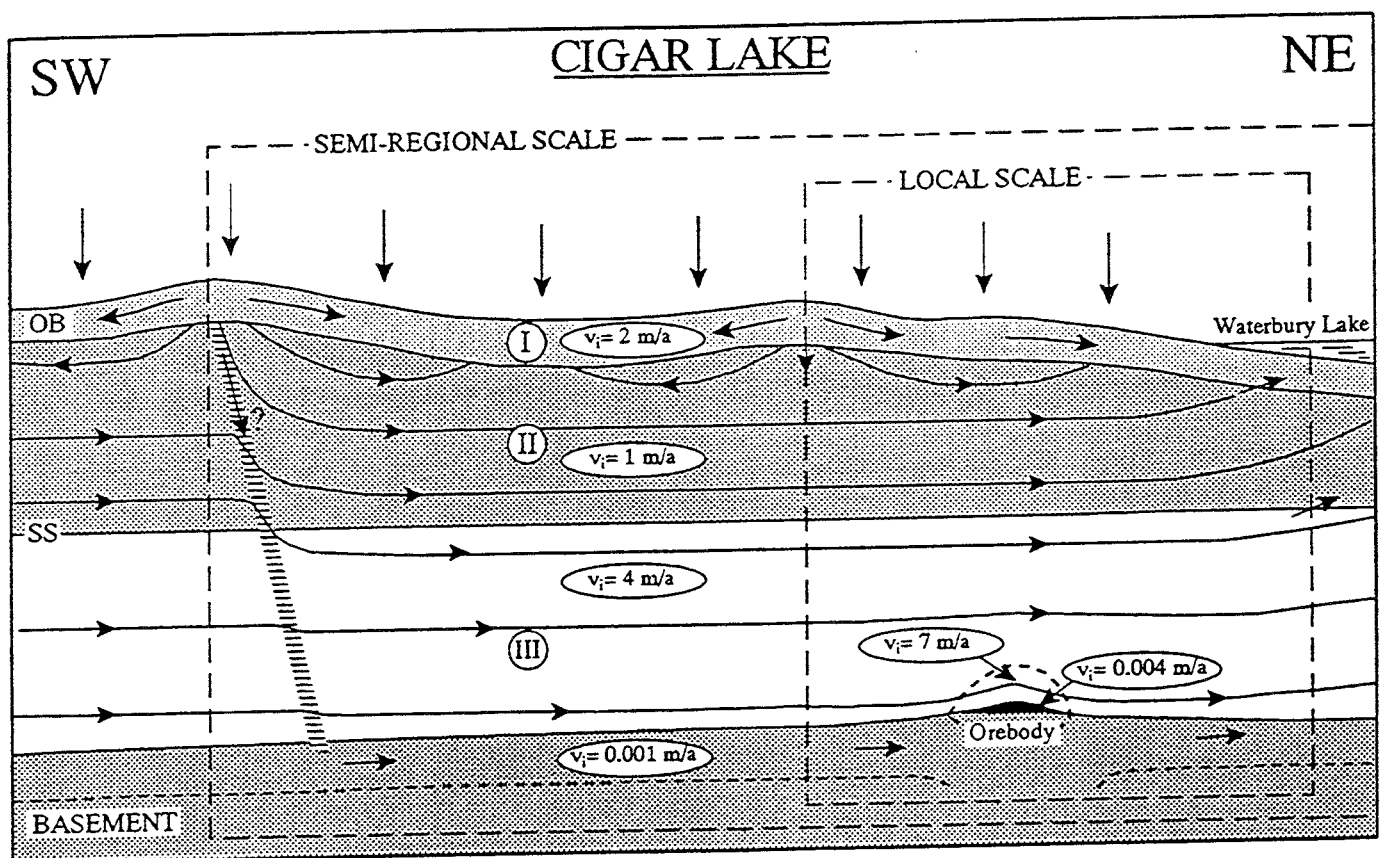along the proposed groundwater flow pathways.

Figure 5.1: Schematic vertical 2D section through the Cigar Lake deposit showing defined flow regimes, their calculated particle velocities and their interaction. I = shallow Local Flow Regime, II = Intermediate Flow Regime and III = deep Semi-Regional Flow Regime. An example of recharge along a fracture zone is schematically illustrated in the left side of the diagram (after Winberg and Stevenson, 1994).

5.1.2   Hydrogeology

Specific points addressed concerned the usefullness of the 2D and 3D models employed and whether the heterogeneity of the system has been adequately considered in the modelling. Winberg (1995a) has reappraised the amount and quality of data available and possible improvement on interpretation of the earlier modelling results.

The modelling approaches employed at Cigar Lake were based on a layered porous medium. This approach may appear inappropriate since the hydraulic test results and observations of piezometric disturbances from the underground activities indicate an overall heterogeneous groundwater flow medium, at least in the immediate vicinity of the orebody where fracture controlled flow is almost certainly operative. Fracture network modelling of the system, however, was not possible because of a lack of fracture size statistics in the database. The fact that the test-sections are highly variable in length (3-45 m) makes it difficult to infer fracture transmissivities. Likewise, this variability makes it difficult to evaluate the data for use with a stochastic continuum model. Ideally, the data used for statistical fracture inference (univariate statistics and covariance structure) should be at the same scale, i.e. from the same test-section. A further complication is that the various hydraulic units should probably be treated separately, but again the amount of available data from each unit is too small to facilitate fracture inference (Winberg, op. cit.).

It was pointed out that the 3D model had not been successfully calibrated in the transient stage using existing interference test results. The model, however, did not deviate dramatically from existing previously calibrated flow models of the area. Hence, the delineation of flow regimes, hydraulic gradients, residence times and discharge points for the groundwater are considered realistic.

In summary, whilst some fine adjustments to the 2D and 3D models could have been made, the main problem concerned a lack of additional data, specifically more sensitive downhole hydraulic testing which may have provided greater insight into the extent of fracture flow in the vicinity of the orebody. This in turn would have provided some important conceptual input into the mass transport models directly linked with performance assessment issues. Despite this, the present status of hydrogeological modelling is considered adequate to accomplish a broad conceptual understanding of the Cigar Lake groundwater flow system, and to provide enough input data to satisfy the major performance assesssment objectives of the study.

5.1.3   Coupling of hydrogeology and hydrochemistry

The local scale (1200 m) conceptualised groundwater flow system at Cigar Lake is generally quite simple. According to Winberg and

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Stevenson (1994), the results showed the development of three flow regimes; a) superficial regime with predominant flow in the overburden and the upper part of the weathered sandstone, b) an intermediate flow regime with water recharging in the upstream end, partly discharging into Waterbury Lake and partly feeding the lower sandstone, and c) a lower semi-regional regime that comprises water in part recharged beyond the limits of the modelled system, and in part being fed by water percolating through the overlying strata mostly via discrete fracture zones. The semi-regional groundwater flows primarily within the Lower Sandstone; final discharge for all regimes is Waterbury Lake as suggested by tracking of water particles from the local model into the regional model. Groundwater flow at the depth of mineralisation is horizontal, from south to north, with an average hydraulic gradient of approx. 1%.

The above conceptual model is supported by groundwater chemical and isotopic trends which generally support a systematic evolution of groundwater chemistry with increasing depth along the modelled flow paths. However, anomalous increases in TDS content (e.g. Na; K, Cl) become apparent towards the sandstone-basement contact. This was initially interpreted as resulting from the mixing of more dilute downward percolating recharge waters with a minor basement groundwater component (Pettersson, 1992). As mentioned in subsection 3.1.1, however, Cramer and Nesbitt (1994) consider the increase in TDS as resulting from ancient salts of hydrothermal origin (i.e. coeval with ore formation) released by present groundwater reaction with the mineralised zone and surrounding altered host sandstones. This was supported by whole-rock leaching studies which showed a close correlation between formation groundwater and leachate compositions. They also pointed out the very low hydraulic conductivity of the basement, and the fact that there is no other hydrogeological evidence to support groundwater flow occurring from basement to sandstone. The former statement is supported by modelled particle velocities for the various stratigraphic/hydraulic units (Winberg and Stevenson, 1994) which show almost four orders of magnitude contrast in particle velocity between the basement (v_i =0.001 ma^{-1}) and the altered sandstone (v_i =7 ma^{-1}) (Fig. 5.1).

Present studies have focussed on treating the groundwater database by applying established statistical and mathematical methods of data evaluation to highlight groundwater evolution patterns, for example, multivariate analysis and the use of Piper and Stiff diagrams, and also attempting to define the geochemical evolution of the groundwaters using kinetic mass transfer models. As each method addresses different geochemical characteristics of the groundwaters, they should be viewed separately rather than compared. These approaches were mostly carried out as simple "blind" modelling exercises; with one exception (kinetic modelling) neither of the other two groups had prior experience or knowledge from the Cigar Lake study. Figure 5.2 shows the location of the borehole sections sampled for groundwaters used in this evaluation.
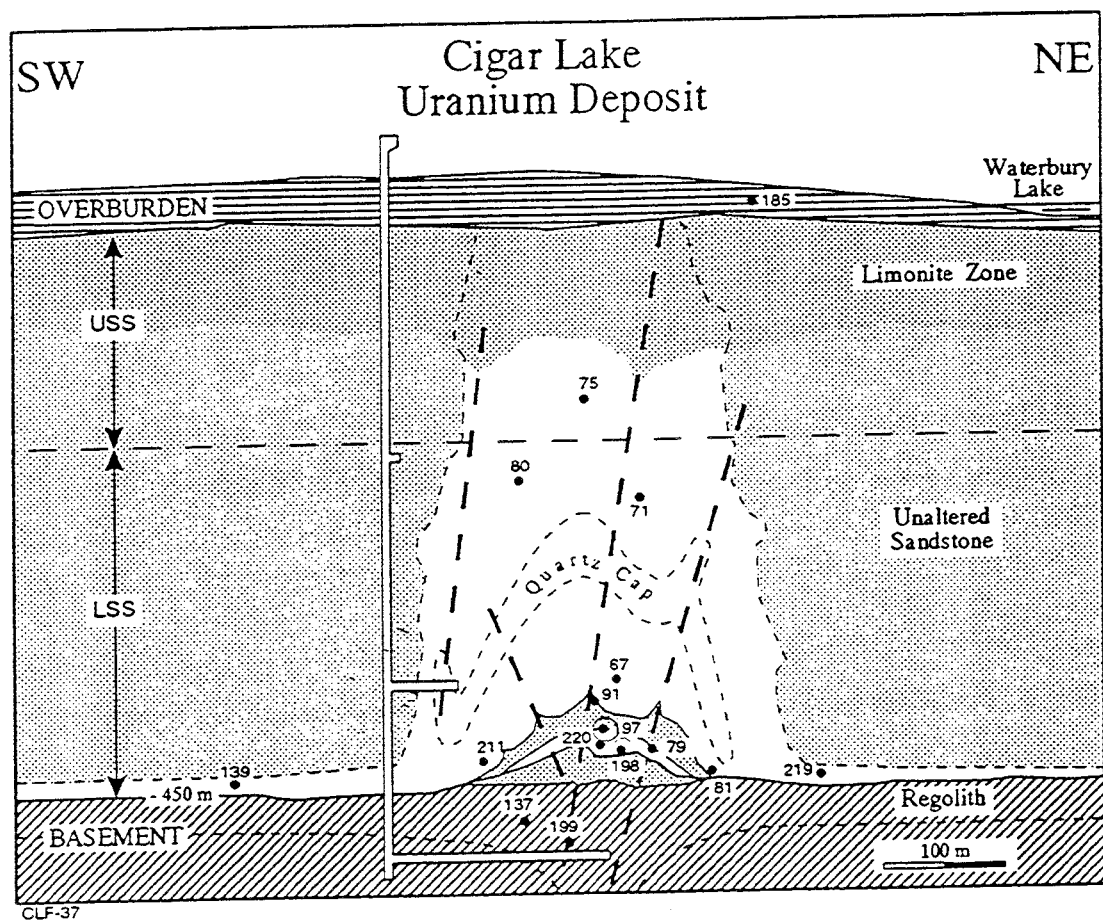
Figure 5.2:   Schematic vertical section through the Cigar Lake deposit
showing the locations of the sampling points discussed in the
text (after Cramer and Nesbitt, 1994).

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Piper Diagrams

Possible mixing between basement and recharging dilute groundwaters was initially suggested by Pettersson (1992) after plotting the major chemical components in a standard Piper diagram (Fig. 5.3). The figure shows compositional separation between basement (borehole 199), ore (borehole 220), clay (borehole 91) and dilute sandstone groundwaters (boreholes 75, 139, 81 and Waterbury Lake). The remaining waters plot within the central part of the diagram suggesting differential mixing proportions between the dilute sandstone groundwaters and the basement type.
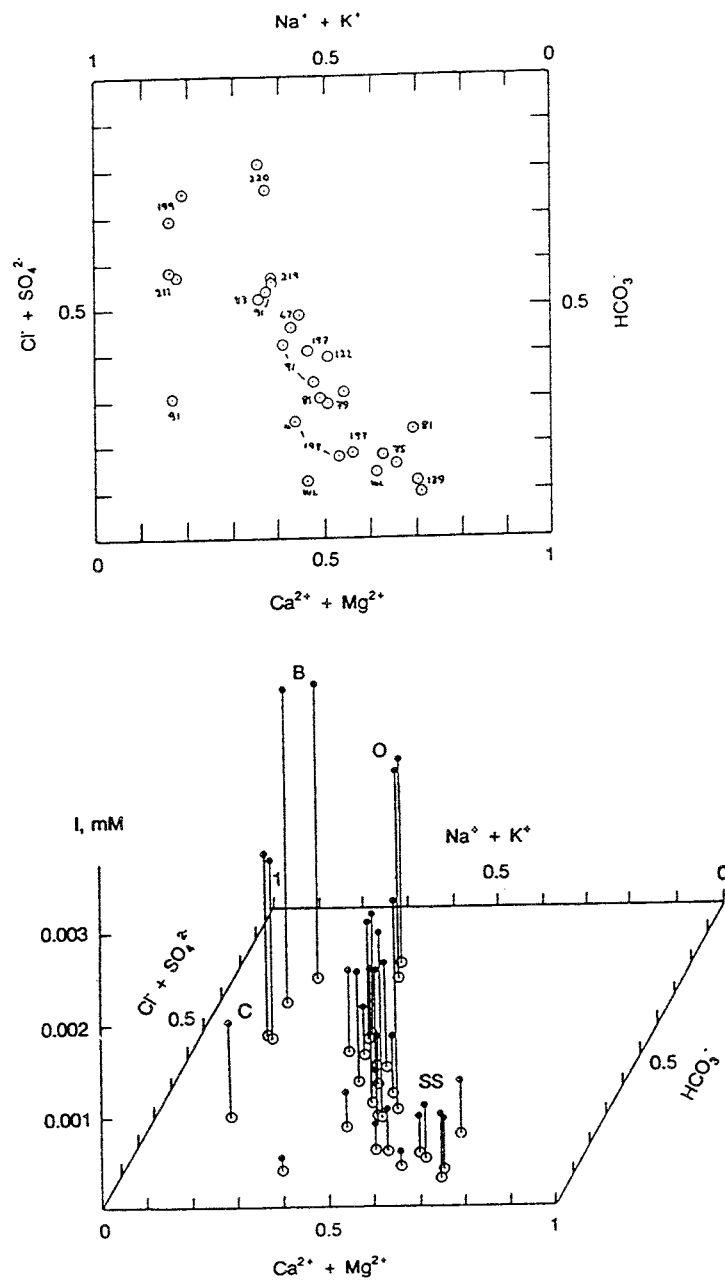
Figure 5.3:   Piper Plot of the major components in the sampled groundwaters (B = basement; O = ore; SS = sandstone)

Stiff Diagrams

Stiff diagrams (Appelo and Postma, 1993) are constructed by recalculating the groundwater components into milliequivalents per litre and then plotting the main cations and anions as shown in Figure 5.4; graphically it is a very convenient method to illustrate variations in groundwater composition. Stiff plots for each sampled location are illustrated in Figure 5.5 (Grundfelt et al., 1995), and the following conclusions can be drawn:

* similar chemical patterns between water samples from the upper sandstone and the overburden indicate a good hydraulic communication between the two regimes,

* groundwater in the lower sandstone appears to be a mixture of waters from the overburden via the upper sandstone and groundwater from the basement. The influence from the basement increases in the basal part of the lower sandstone regime. With increasing distance from the basement, the predominance of the overburden water characterises the chemical composition,

* some groundwater samples from the clay and ore zones show a possible hydraulic communication along some fractures between groundwater from the basement and water from the overburden and upper sandstone. The resulting groundwaters from the clay and ore zones in these samples appear to be different mixtures of basement water and water from the overburden via the lower and upper sandstones.
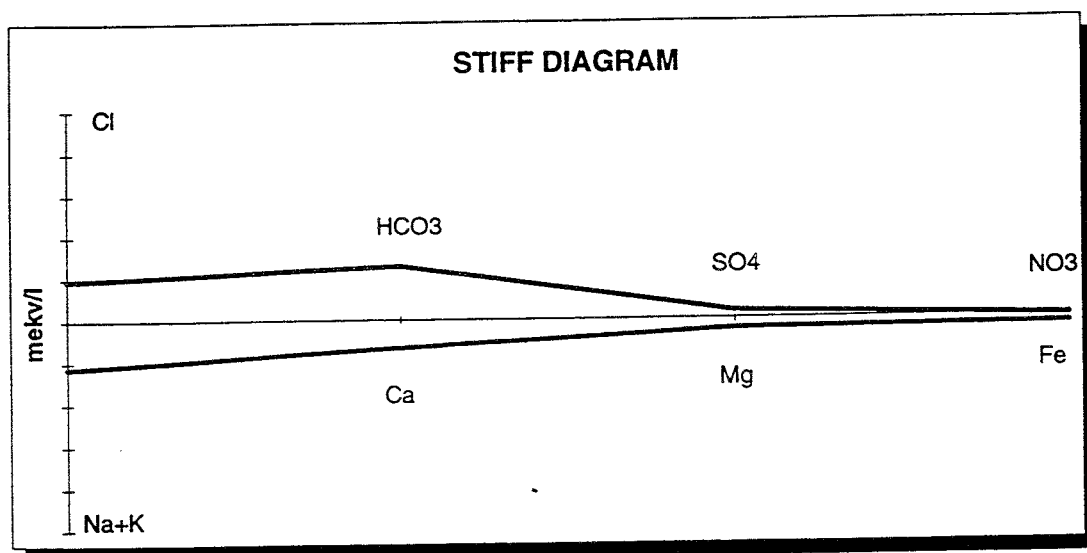

Figure 5.4: Example of a Stiff diagram, calculated from one of the reference groundwater compositions
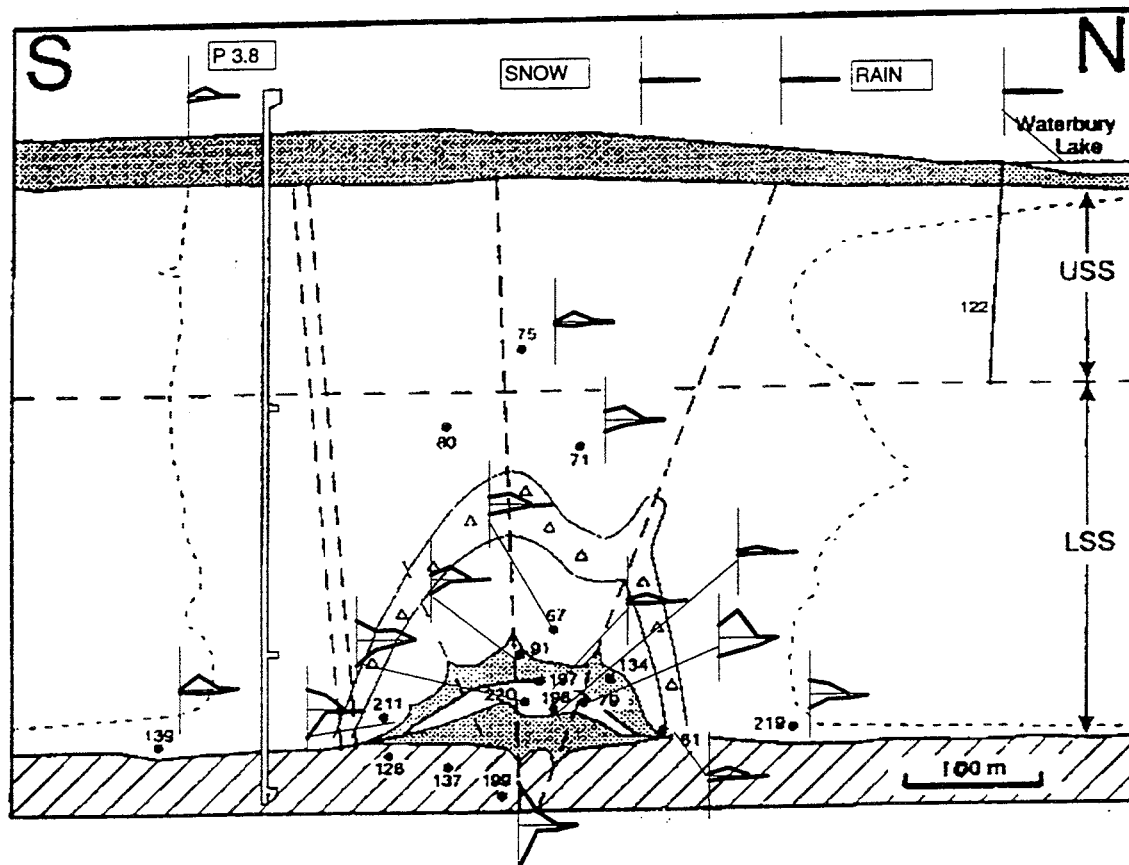
Figure 5.5:   Schematic vertical section through the Cigar Lake deposit showing the relative position of the sampling localities and the corresponding Stiff diagrams for some of the reference groundwaters.

Kinetic Mass Transfer Modelling

Duro and Bruno (1995) have applied kinetics to the geochemical modelling of the Cigar Lake system, specifically at the clay/ore interface (Chapter 3). Calculations have supported the evolution of groundwater chemistry within the altered sandstone above the clay contact, i.e. from borehole 211 through boreholes 91, 67 and 197 to 81, and also an evolutionary mixing profile from recharging dilute water (borehole 71) to basement compositions (borehole 199).

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Multivariate Mixing and Mass Balance Calculations

The aim of this exercise was to use multivariate statistics on the Cigar Lake hydrochemical data in order to identify possible groundwater flow and evolution paths. In contrast to more traditional methods of groundwater classification (see above), multivariate analysis can distinguish between mixing and reaction processes

To establish the effect from mixing and reactions in the groundwaters a *Multivariate Mixing and Mass balance* (M3) model was constructed (Laaksoharju et al., 1995; Laaksoharju and Skårman, 1995). The model describes the portions of particular types of water needed in order to explain the chemical composition of an observed water type. The deviation from the model is due to mass balance reactions. The mixing processes are inherently very complex and include multi end-member mixing processes. A multivariate method called Principal Component Analysis (PCA) was therefore used. The strength of this approach is that all variables in a data matrix can be examined simultaneously. Greater resolution is possible and the character of the data in a general data matrix is therefore more easily identified than using univariate analysis, where only one variable is compared at a time. The major components Cl, Ca, Na, Mg, K, SO_4 HCO_3 and the isotopes ^3H, ^2H and ^{18}O were used in the PCA. It is important to note that both conservative and non-conservative elements were used. This is possible since conservative or non-conservative behaviour in one or several of the variables can be tracked by PCA.

The result of the analysis and the identified end-members are shown in Figure 5.6. The selected end-members represent extreme waters found in the Cigar Lake site. Figure 5.6 show that water sampled near the ore/clay interface (borehole 79 in Fig. 5.6) may act as a *deep end-member* in the system. The water in the upper sandstone (borehole 75 in Fig. 5.6) may then act as a *shallow end-member*. The water in the lower sandstone and in the clay may contain input from both shallow water and deep water (borehole 71 in Fig. 5.6) and represents a *mixed water end-member*. The water sampled from the orebody in borehole 220 seems to contain a different water type not found elsewhere. This water was considered as an *ore water end-member*.

The four identified end-members form a quadrant. The observations within the quadrant can by definition be described by the selected end-members. The co-ordinates for the observations are given by the first and second Principal Component respectively (Component 1 and Component 2; Fig. 5.6). The scales in Figure 5.6 are linear and the distance from any observation to the five end-members can be calculated by using simple trigonometric functions, i.e. the quadrant is used as a phase diagram. As the distance is equivalent to the mixing ratios of any water observed in the system, the exact mixing portions of any groundwater sample can be
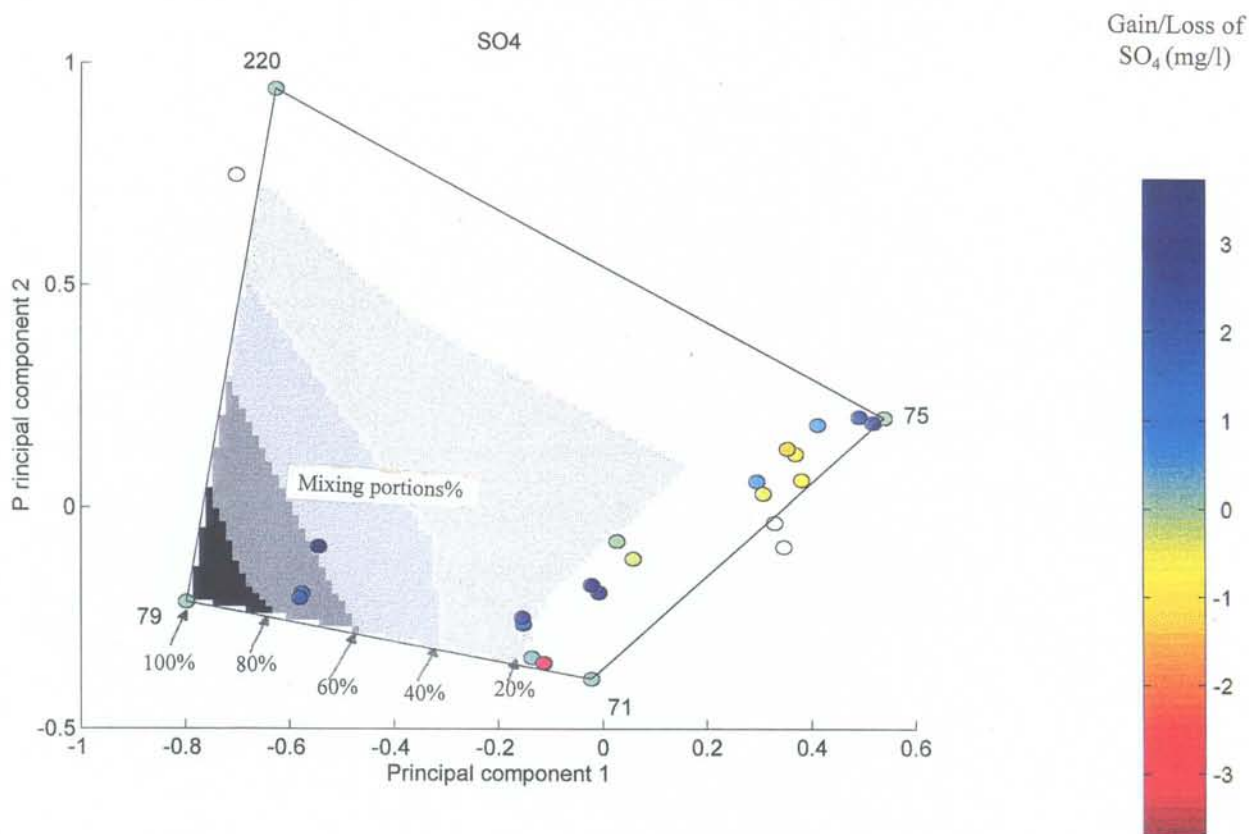
Figure 5.6:   A Principal Component plot showing the data from Cigar
                    Lake based on the variables Cl, Na, Ca, K, Mg, SO$_4$ HCO$_3$, U,
                    ^{3}H, ^{2}H and ^{18}O. The possible mixing portions of 100-80%, 80-
                    60%, 60-40%, 40-20% and 20-0% of the deep groundwater
                    type (79) are shown. The mixing portions can be used to
                    predict new values for a species such as SO$_4$. Sources or sinks
                    (Gain/Loss) from the prediction are due to mass balance
                    reactions. The first principal component describes ~50% of the
                    variability in the data; the first and second principal
                    component together describes ~80% of the variability, or most
                    of the information represented by the data.

calculated. The mixing portions can be used to predict values for any groundwater element included in the model. The predicted value is compared with the measured values; deviation (gain or losses) is due to mass balance reactions.

The influx of the deep end-member water (borehole 79) has been modelled (Fig. 5.6). The calculations show that the shallow waters in the sandstone (i.e. boreholes 71 and 75) are affected in portions of less than 20% by the deep groundwater. The sources and sinks (gain/loss) for the element SO_4 have been superimposed. Sulphate was chosen simply to exemplify the degree of mixing between the deep and shallower groundwater end-members. The source of sulphate is found in the deep groundwater end-member and the sink is in the shallow groundwater end-member. The sinks and sources for other elements show a similar pattern, indicating that the deep groundwaters have a different element behaviour when compared with the more shallow groundwaters. The deeper groundwater therefore is a distinct type with a _different evolution_ when compared to the shallow waters. Mixing of these two types would occur to a _minor extent_ if there is any hydraulic connection.

5.1.4 Summary and Discussion

The Cigar Lake reference groundwater compositions have been evaluated by four different approaches based on identifying groundwater groups of similar chemistry (i.e. of similar possible origin) and identifying potential evolutionary trends (reaction and/or mixing profiles) along groundwater flow pathways as indicated by the hydrogeological model. In all cases, to varying degrees, the main trend is shown by recharging dilute waters of overburden type and their subsequent progressive evolution with increasing depth towards the mineralisation. Peripherally and within the mineralised zone (i.e. near the Lower Sandstone/Basement contact) there is an increase in TDS content consistent with variable mixing with groundwaters of basement composition.

Grundfelt et al. (1995) addressed the hydrogeological evidence to support the chemical evolution of the groundwaters. By comparing seasonal piezometric variation between individual sampled boreholes (Fig. 5.7) it was possible to confirm a strong downward hydraulic recharge gradient (i.e. from borehole 75 to 67) characterising the total sandstone sequence, but also some indication of a upward flow component (inferred gradient in the order of 0.5%) from the altered basement into the clay/ore zone (i.e. from borehole 199 to 197). These gradient trends would adequately explain many of the observed mixing variations illustrated by the classification methods described above, in particular the possibility of a basement component.

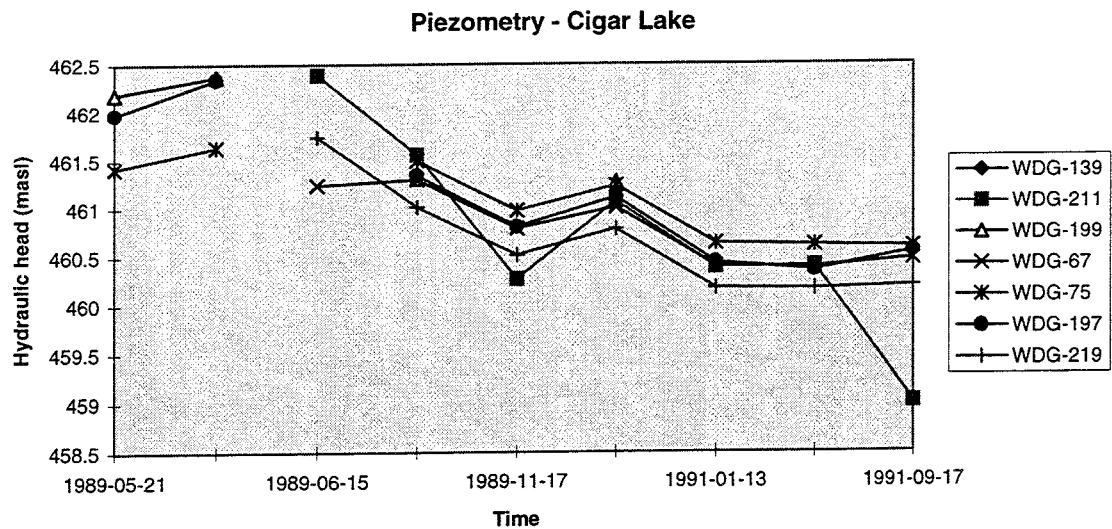**Piezometry - Cigar Lake**

Figure 5.7:   Variation of piezometric levels among some of the reference groundwaters in the vicinity of the ore.

Basement to sandstone groundwater flow was not indicated from earlier modelling studies by Winberg and Stevenson (1994), and has been subsequently criticised by J.J. Cramer (written comm. 1994) who pointed out that no evaluation of the volumetric quantities of basement water necessary to produce the observed compositions has been carried out. Moreover, he doubted whether the hydraulic gradient was sufficient to explain the water compositions in borehole 71. This latter issue, however, as with some other anomalous compositions recorded, may also be explained by short-circuiting water from depth via connecting fracture zones during sampling. The basement and the overlying mineralisation are characterised by considerable fracturing, most of which have been sealed by clay formation coeval with mineralisation, but others are presently water conducting as suggested from water/rock interaction studies (Smellie et al., 1994).

Cramer and Nesbitt (1994) have discussed the problem of increased TDS in length, considering four possibilities: a) basement flow component, b) residual hydrothermal formation waters in the mineralised sandstones, c) contribution from fluid inclusions in the mineralised sandstones, and d) contribution from the leaching of residual salts of hydrothermal and

diagenetic origin present in the sandstones. Possibility (a) was considered unlikely because of the lack of hydrogeological evidence, and that pH, ^{3}H and TOC etc. in the Lower Sandstones could not be reproduced only by mixing with a basement component. Mixing as a result of (b) could explain the stable isotopic signature but not the major ion composition, whilst (c) would require a minimal contribution from fluid inclusions to reproduce the major ion compositions, too small in fact to explain the variation in stable isotopic signatures. According to Cramer and Nesbitt (op. cit.) possibility (d) is the most feasible explanation compatible with the major element compositions and the isotope data.

In summary, the main developments since the earlier studies have been: 1) there is now some hydrogeological support for an upward basement flow component to the overlying sandstones, 2) the various classification methods have indicated mixing trends between the basement and recharging dilute groundwaters, and 3) there is some suggestion of a kinetic mass transfer reaction pathway between basement and recharging groundwaters. Equally, if not more important, a contributary factor to groundwater mixing may be an artefact of downhole sampling methods. This is partly indicated by ^{14}C-dating of organic material which showed a "modern" age for groundwater collected from borehole 197 at the ore/clay interface (see Section 5.3). Although none of these developments shed any doubt on the leaching of a residual hydrothermal salt source to explain groundwater compositions in and around the ore zone, as advocated by Cramer and Nesbitt (op. cit.), they still lend credence to a basement groundwater input that should not be overlooked.

5.2 THE CIGAR LAKE PALAEOSYSTEM

Within the Cigar Lake project little emphasis was put on palaeo-evidence of past bedrock and groundwater conditions (e.g. climate variation; erosion/uplift etc.) that may have influenced the evolution of the Cigar Lake uranium deposit since its formation. This may be explained by several reasons. For example, the standard use of environmental isotopes to evaluate groundwater evolution and residence times has been complicated by the near-vicinity of the orebody which produces, by *in situ* production, many of the radioactive isotopes otherwise used as groundwater tracers (e.g. ^{14}C, ^{3}H, ^{36}Cl). Groundwater residence times have been estimated by surface-release particle simulations (Winberg and Stevenson, 1994) which suggested, for the reference case, residence times in the order of 800-1 000 a. This indicates that the groundwater turnover within the host sandstone is too rapid (hundreds of years) to have retained any widespread ancient groundwater signatures.

In contrast, simulations of particles released from the ore zone indicated

groundwater residence times of 18 000 to 85 000 a, which is in general agreement with residence times calculated from *in situ* ^{36}Cl data (Cornet and Cramer, 1994).

In this present reappraisal of the palaeosystem, two areas of interest to repository performance assessment were addressed: determination of the water/rock ratio at Cigar Lake at the time of ore formation, and the downward rate of movement of the limonite zone ("redox front propagation") since the last glaciation.

5.2.1 The Cigar Lake Palaeosystem: Estimating the Water-rock Ratio

The effective water/rock ratio is an important parameter in determining the equilibrated mineral assemblages during ore formation, aqueous speciation, and Eh-pH conditions (see Section 2.3). The ratio is in part governed by the hydraulic characteristics of the formation, i.e. the hydraulic conductivity and porosity (distribution) and flow velocity (distribution) (Winberg, 1995b).

This ratio is known from the present-day stratigraphic and hydrogeological environment of Cigar Lake. However, to successfully predict the influence of geological processes on the stability of the orebody (i.e. "repository") over future geological timescales, it is necessary to understand the boundary conditions prevailing at the time of ore formation. The present-day sediment cover at Cigar Lake is approx. 450 m; estimates at the time of ore formation are put at 3 000-5 000 m (Ramaekers, per. comm., 1994). Little is known, however, about the influence of this sediment cover on the hydraulic character of the lower sandstone, i.e. what ranges of hydraulic conductivity and porosity etc. prevailed at that time? Furthermore, to assess the natural flow velocity at the depth of the orebody, the hydraulic driving force (hydraulic gradient) controlled by surface topography, must also be estimated. In this respect the palaeotopography is considered to have been more flat than today. Consequently, the hydraulic gradient at that time was even less than indicated by the palaeotopography, given the gradient attenuation suggested from the large thickness of the sediment pack.

In order to assess the hydraulic conditions in the Lower Sandstone at the time of ore formation, Winberg (op. cit.) estimated the hydraulic conductivity and porosity of the palaeosystem on the basis of petrophysical parameters. Many of these data are available from earlier geotechnical studies carried out as part of the exploration campaign. Calculations (Fig. 5.8) indicated a palaeo-porosity in the order of 20%; a comparison between this figure and present-day porosity, as determined from indirect *in situ* measurements on core material, showed values of the same order. Furthermore, if it is assumed that the hydraulic conductivity is linearly related to the porosity, then it can be assumed that the hydraulic conductivity of the lower sandstone in the palaeosystem should

have been of similar magnitude as that experienced today.

Estimation of the hydraulic gradient at the depth of the orebody during formation is complicated by two unknown factors: 1) the palaeo-topography, and 2) how the gradient is attenuated with depth. The present-day gradient has been calculated at 0.3%, whereas the gradient at the time of ore formation is estimated at $1 \cdot 10^{-5}$.
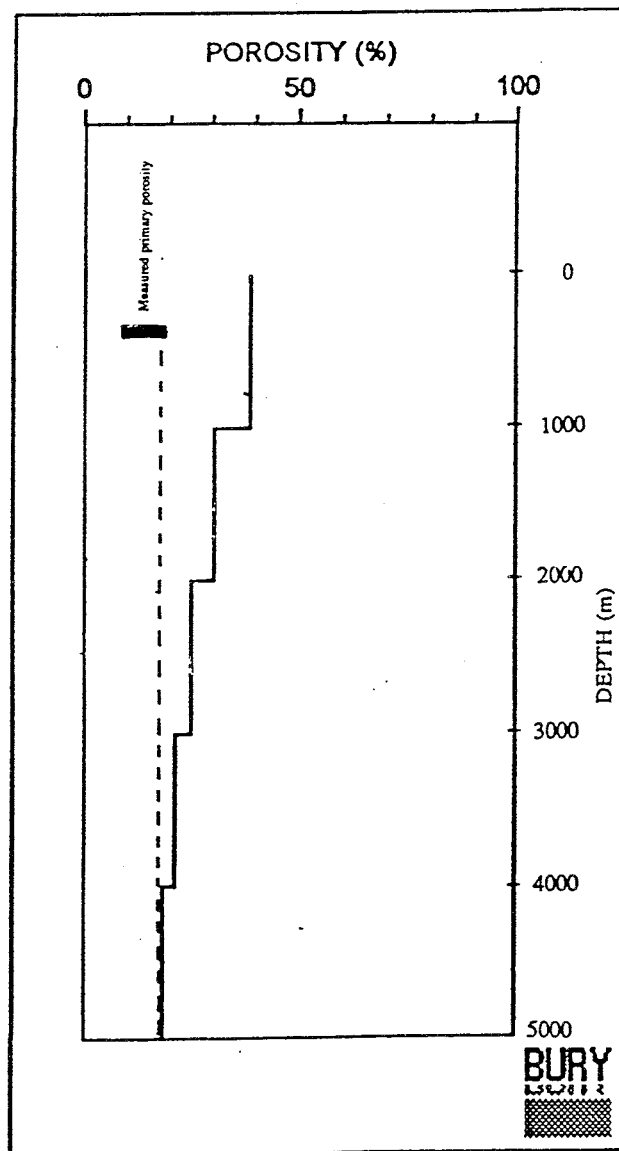

Figure 5.8:   Calculated primary (granular) porosity as a function of depth for a rock type similar to the Lower Sandstone at Cigar Lake (sand 85%, p= 2650; clay 15%, p= 2450)

As reasonable approximations of the Cigar Lake palaeosystem at the time of ore formation, Winberg (op. cit.) has suggested the following numbers which may be used as input into predictive modelling exercises:

Porosity $\phi_{lower\ sandstone}$ $= 20\%$

Hydraulic conductivity $K_{lower\ sandstone}$ $= 5 \cdot 10^{-6}$ m/s

Flow velocity $v_{lower\ sandstone}$ $= 5 \cdot 10^{-11}$ m/s

5.2.1   Redox Front Formation

The upper part of the sandstone host rock comprises a limonite zone (Limonitic Upper Sandstone; Fig. 5.2) characterised by iron staining which results from the oxidation of pyrite and marcasite to produce limonite and goethite (Cramer and Nesbitt, 1994). The limonite zone is slowly moving downwards (probably driven by erosion rates) and has reached a depth of approx. 100 m. This "oxidation front" indicates that oxidising groundwaters have permeated to this depth, at least since the last glaciation 10 000 a ago, but the limonite zone may also have been subjected to earlier glaciations, now masked by the most recent event, suggesting total timescales in the order of 1 Ma.

Grundfelt et al. (1995) studied these redox processes as an analogy to the the formation and propagation of redox fronts around a waste canister resulting from radiolysis reactions. They concluded with the following observations, which are in broad agreement with the earlier studies carried out by Cramer and Nesbitt (op. cit.):

* the redox chemistry is determined by the $Fe^{2+}/Fe(OH)_3$ and S^{2-}/SO_4^{2-} redox couples,

* there is a continuing process of oxidising water from the overburden penetrating into the sandstone formations, along fractures and through the permeable sandstone,

* the oxidation front has penetrated approximately 100 m into the sandstone, causing oxidation of pyrite and marcasite to limonite and sulphate,

* the oxidation of pyrite to limonite and sulphate results in acidification of the groundwater,

* this process has been on-going at least since the last glaciation (10 000 a); in the upper parts of the limonite zone the duration is probably much longer, reflecting past glacial epochs (possibly to 1 Ma ago), and

* the long-term stability of the uranium mineralisation can be influenced

by the movement of the redox front due to increased uranium mobility.

5.3 RADIONUCLIDE TRANSPORT: ROLE OF ORGANIC MATERIAL

Ephraim et al. (1995) carried out a comparison of existing Cigar Lake data (Pettersson et al., 1994) with selected sites studied within the Swedish radioactive waste programme. The concentration of natural organic material (TOC) in the Cigar Lake groundwaters sampled to depths of around 480 m, ranged from 0.63 to 13.2 mg/L. The percentage of humic substances, unrelated to the amount of TOC, was 1-25%, mainly constituting fulvic acids of low molecular weight. Apart from their smaller sizes, the fulvic acids from Cigar Lake have typical characteristics (i.e. trace elements; acidity) comparable to fulvic acids from Swedish sites (Table 5.1). The fulvic acid from the ore zone area was dated by ^{14}C to be very old (15 000 a), which contrasted with "modern" samples collected close by, suggesting possible contamination from borehole activities. A combination of the total concentrations of organic material and the interaction affinity for uranium indicates that the speciation of uranium will not be significantly affected by organic acids. Such a prediction is corroborated by the low concentrations of uranium measured in the organic acids fraction (i.e. 0.36-0.98 mg/g; Pettersson et al., 1994).

Table 5.1: Characteristics of fulvic acid isolated from the Cigar Lake groundwaters, compared with Swedish site areas.

Sample	Country	Origin	Depth (m)	M_n	M_w	Acidity (meq/gFA)	^{14}C-Age yrs
Bersbo	Sweden	Bogwater	0	1750	2650	4.65	N.A
Vadstena	Sweden	Limestone	40	850	1050	5.46	N.A
Äspö	Sweden	Granitic rock	75	1520	1920	9.86	640
Fjällveden	Sweden	Granitic rock	409	1250	1700	5.14	1270
Cigar Lake 83	Canada	Sandstone	18-477	760	1030	3.78	modern
Cigar Lake 197	Canada	Clay	418	680	860	5.26	modern
Cigar Lake 79	Canada	Uranium ore	431	630	720	5.44	15330
Cigar Lake 139	Canada	Sandstone	441	860	1100	3.31	N.A.

RADIONUCLIDE TRANSPORT: ROLE OF MICROBES

Earlier microbial studies at Cigar Lake were restricted to establishing the presence and quantity of microbes and, in some cases, identifying and subdividing the major aerobe and anaerobe types into sulphate reducers, iron-related, denitirifiers, fermenters and methanogens (Stroes-Gascoyne et al., 1994). As part of this reappraisal study, Pedersen (1995) has discussed the role of microbes in general, raising the following points:

* What types of bacterial processes, if any, dominate in the Cigar Lake site?,

* What influence have these bacterial processes on the geochemical situation at Cigar Lake?

* Which bacterial processes in Cigar Lake relate to performance assessment?

The first two points are not addressed in detail because of a lack of relevant published data. In the light of repository performance assessment, Pedersen (op. cit.) addressed the potential influence of bacteria in relation to: a) stability of UO_2, b) reduction of U(VI), c) recombination of radiolysis products, d) oxidation of Fe(II) compounds, e) oxidation of reduced sulphur compounds, and f) oxidation of organic material. Within each of these categories it can be demonstrated that bacteria can play an important role. Moreover, sufficient bacteria and the right types of bacteria exist at the Cigar Lake site. The two most interesting points addressed, which link in directly with earlier discussions in this report, are the potential influence on recombination of radiolysis products and the oxidation of Fe(II) compounds.

Regarding the bacterial recombination of radiolysis products, Pedersen (op. cit.) presented the theoretical background and compared chemical and bacterial oxidation processes. He concluded that reactive radiolysis products may very efficiently be converted to oxygen by aerobic and facultatively anaerobic bacteria. The hydrogen produced during radiolysis, together with the oxygen produced from reactive oxygen species, can subsequently be recombined by bacteria during the formation of organic material, heat and water. Energy from radioactive decay may in fact be partly conserved as organic material in the form of bacteria. This is an alternative or complementary model for the fate of radiolysis products. Results from Cigar Lake have shown that the bacteria are present and that there are also measureable amounts of organic material ranging between 0.9 up to 7 mg/L. The presence of this bacterial process is advantageous to performance assessment since it will contribute to the stability of U(IV) by reducing the potential effects of radiolysis, and thereby reducing the oxidative effect from such compounds.

In the second example, the oxidation of Fe(II) compounds by bacteria, Pedersen (op. cit.) points out that as iron-related bacteria have been identified at Cigar Lake, then iron-oxidising bacteria may also be active. If this is the case, then these bacteria may be able to catalyse the oxidation of ferrous species from outside the ore with oxygen produced by radiolysis from within the ore. Such activity would be present along the gradient between reduced and oxidised conditions, producing a diffuse zone of ferric precipitates rather than a sharp redox front. This could be an additional explanation to the zone of enhanced iron content in the clay near to the massive ore contact, to those discussed under Sections 2.3, 2.4 and 4.1.

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6. CONCLUSIONS AND PERFORMANCE ASSESSMENT IMPLICATIONS

6.1 BACKGROUND

Features, events and processes (FEPs) represent the most basic components used to describe the evolution of a repository system. According to Anderson et al. (1989): "In principle, the safety analysis of a radioactive waste respository involves the consideration of all possible relevant FEPs that could, directly or indirectly, influence the release and transport of radionuclides from the repository". To help demonstrate the occurrence of such FEPs in nature and to suggest how they may be combined into "scenarios" for quantitative analysis, evidence from natural analogue studies has sometimes been used. Within specific scenarios, natural analogues are often used to support model assumptions, particularly for the case of engineered barrier longevity (e.g. bentonite stability).

The systematic development of scenarios by first identifying and collecting a large number of Features Events and Processes (FEPs) considered important to the isolation of radioactive waste, was first developed at the Sandia National Laboratories in Albuquerque, USA. The method was further developed in Sweden (Andersson et al., 1989) and a FEP list for the Swedish concept for spent fuel disposal was presented by a working group consisting of members from both the Swedish Nuclear Fuel and Waste Management Company (SKB) and the Swedish Nuclear Power Inspectorate (SKI). The method to identify scenarios from FEPs via the construction of a Process System was introduced and highlighted. The Process System was described as "the organised assembly of phenomena (FEPs) required for the description of barrier performance and radionuclide behaviour in a repository and its environment". A scenario is then defined by a specific set of external conditions that will influence FEPs in the Process System.

Different methods have been used to visualise and structure the Process System. A "reversed event tree" was initially used in the final safety assessment of the Swedish repository for low- and intermediate-level waste (SFR). The method of constructing Influence Diagrams was used at least twice; by the authorities, SKI, in their performance assessment study of a generic site (Site 94), and by SKB in the preliminary study of barrier functions of a repository for long-lived low- and intermediate-level waste. A third method, the RES (Rock Engineering System), has recently been developed. In this approach the most important FEPs (e.g. fuel stability; bentonite stability; canister stability etc.) for a repository system are arranged diagonally in a matrix diagram. The adjacent squares in the matrix allow the interactions (e.g. tectonics; hydrogeology;

hydrochemistry etc.) between the major FEPs to be followed. All three methods have recently been compared by Eng et al. (1994).

The use of natural analogue studies to support and describe FEPs has sometimes been referred to as the "indirect or hidden use" of analogue data (Smellie et al., 1995). A good example is radiolysis; radiolysis of water at the exposed surface of spent fuel is very difficult to calculate. Furthermore, experimental results have been so rare that the conclusions and evaluation of this phenomenon are to a large extent based on observations from analogue studies, for example, the Oklo natural reactors and the Cigar Lake uranium occurrence.

Studies at Cigar Lake have identified several FEPs of importance to scenario development and repository performance assessment: The three most important are radiolysis, clay buffer and fuel dissolution.

6.2   RADIOLYSIS

6.2.1   Model Development

Radiolysis was early recognised as a potential problem for the Swedish disposal concept (KBS-3, 1983). At that time oxidising conditions, as a result of alpha-radiolysis of water, where assumed for the spent fuel leaching scenario and a simple mass balance model was used to conceptualise the effects of radiolysis reactions at the repository near-/far-field interface. This model predicted that excessive radiolysis may result in the transport of uranium and other oxidising species in association with a propagating redox front away from the spent fuel, through the bentonite overpack, and out into the surrounding rock. However, the natural redox buffering capacity of the bentonite and rock (e.g. mainly due to Fe^{2+} contained in the mafic mineral phases) is expected to restrict the movement of the redox front. Radionuclides mobilised and transported by the oxidants would precipitate along, or at the reducing side of these fronts.

How realistic was this concept of redox front propagation? Confirmation was obtained in 1984 from natural analogue studies at the Poços de Caldas site (Chapman et al., 1992) where naturally-occurring, low temperature redox front migration features could be clearly observed and quantified. It was shown that reduction/precipitation mechanisms, as well as scavenging by coprecipitation and sorption, take place at redox fronts. More detailed models were subsequently developed to explain this phenomenon (e.g. Lichtner and Waber, 1992).

Whether adequate oxidants would be available from water radiolysis

reactions at the spent fuel surface, however, was less convincing. Difficulties were being encountered with spent fuel radiolysis experiments because of the very slow reaction rates; consequently, long observation times are needed. There is also a difference in the intensities and relative proportions of alpha, beta and gamma radiation in fresh spent fuel and the very old fuel expected to participate in a release scenario. This subsequently led to a renewed interest in natural analogues, in particular the massive concentrations of very old uranium oxide present at Cigar Lake, Canada (Cramer and Smellie, 1994).

Studies of water radiolysis at Cigar Lake showed that net changes in the ore and near-field were considerably overestimated by models currently used by performance assessment to calculate the yield of radiolysis products (H_2O_2, O_2, H_2) (Karlsson et al., 1994). In an attempt to further refine these models, present studies have established a more theoretical basis (Section 4.1) to understand the geometric radiation dose distributions resulting from single UO_2 grains of different sizes, and established what fraction of the radiation reaches the surrounding aqueous phase to initiate the radiolysis reactions (Jansson et al., 1994; Liu and Neretnieks, 1994). The modelling results show that only a very small fraction of the total radiation energy from a UO_2 grain, irrespective of size, is deposited in the surrounding aqueous phase. These results appear to support the inadequacy of current performance assessment radiolysis models as applied to Cigar Lake where the calculated oxidant production rates are significantly higher. The new approach to calculate radiolysis yields now takes into consideration the importance of the heterogeneity of the alpha energy deposition in water, and although difficulties still remain to be solved, considerable advances have been made in testing and developing a better radiolysis model for use in SKB's performance assessment methodology.

6.2.1 Radiolysis and Redox Fronts

At Cigar Lake the presence of a Fe(III)-rich halo in the clay near to the massive ore/clay interface was initially interpreted as evidence of an outward propagating redox front driven by a continuous supply of oxidants produced from radiolysis reactions of water from within the orebody, a process closely analogous to that expected to happen in the "Reference Scenario Case" following penetration of the copper/steel canister.

The amount of oxidants generated by water radiolysis in the orebody, calculated by models used previously in performance assessment, would certainly be enough to explain the total amount of Fe(III) in the halo. Even the lower production rate obtained by the revised model in this present study is more than enough to account for the ferric iron in the clay. This, however, is considered an unlikely explanation.

In the first case, the groundwater in the orebody has a composition (Eh and pH) which would render Fe(III) effectively insoluble. In addition, particulate Fe(III) will hardly be mobile in the clay. Quite simply, there is no means of transport available for ferric iron. Any oxidants generated by water radiolysis close to the uraninite grain surfaces will therefore have to be inhibited from reduction reactions, such as sulphate to sulphide, to be able to survive the reducing groundwater in the orebody.

In the second case, evidence is provided in Section 2.3 that haematite stablised at a late stage during the hydrothermal formation of the primary uranium mineralisation. As the temperature in the orebody decreased (150-100°C), haematite formation spread pervasively through the orebody and into the surrounding clay. This was demonstrated by theoretical calculations and provides the most likely explanation for the presence of the Fe(III) halo. In other words, the halo represents fossil reactions dating back to the time of ore formation.

Radiolysis reactions, however, may not need to be invoked. One hypothesis considered that the oxidation of Fe(II) to Fe(III) in the clay horizon was initiated by U(VI) released through fluid interation with the uraninites, which were slightly oxidised during ore formation (Section 2.4). This is in agreement with the mineralogical observations and also compatible with the thermodynamic evolution of the ore system. However, this oxidation/reduction mechanism should also result in the coprecipitation of uranium, at least twice as much, in the haematite-rich clay halo. Unfortunately, because of a lack of geochemical data, it was not possible to test this hypothesis by carrying out mass balance calculations.

6.2.3   Radiolysis and Fuel Dissolution

Accepting that the Fe(III) comprising the red-coloured halo is mainly of hydrothermal origin, and that there is no other evidence of large-scale oxidation, for example the removal of massive amounts of uranium or the formation of secondary uranium ore, what comprises the sink for the oxidants generated by water radiolysis? The oxidation of sulphide to sulphate is a possibility and it has been shown (Section 4.1) that the calculated production of water radiolysis products with the new model for radiation deposition are in fair agreement with observed concentrations of sulphate and hydrogen in the groundwater from the orebody.

Section 4.2 discussed the potential effect of water radiolysis (however little) on the stability of the Cigar Lake uraninites as an analogue to the UO_2 of spent nuclear fuel. A ReDuctive Capacity (RDC) model, in principle a function of the total amount of generated radiolytic oxidants and therefore a function of time, was used in the Cigar Lake context to study the dependence of the main parameters (e.g. estimated rates of oxidant generation and degree of uraninite oxidation) with time, thus

deriving an overall expression for the rate of UO_2 matrix dissolution (i.e. spent fuel analogy) over geological timescales, in line with the expected lifespan of a repository system.

Although the modelled results were not dramatic, they showed that the amount of radiolytic oxidant produced was effectively neutralised by the reductive capacity of the UO_2 sites, resulting in slight changes in UO_2 stoichiometry (Eriksen et al., 1995; Bruno et al., 1996). In the Cigar Lake context, it is suggested that the observed oxidation of the uraninites from the orebody probably occurred shortly after the ore formation phase, and the reductive capacity, and hence stability of the orebody (i.e. spent fuel), has essentially remained unchanged since that time.

Other possibilities of oxidant consuming reactions may exist, but the major point is that the calculated oxidant generation rate resulting from water radiolysis can be catered for. It is no longer possible to use the argument that the rate of water radiolysis is still much lower than calculated, at least not based on present Cigar Lake observations.

6.2.4 Main Conclusions

The main conclusions that can be drawn at present is that the models developed to calculate oxidation by water radiolysis are realistic to conservative and will provide a step forward as compared to earlier over-conservative calculations used in performance assessment. An important observation is that conditions can remain reducing if radiolysis is as low as demonstrated in Cigar Lake. In this case oxidants are being consumed close to the ore and the groundwater remains essentially reducing. To draw the analogy with exposed spent fuel, a similar situation would prevent the build-up of a redox front and probably simplify the chemical processes to be considered for radionuclide release. An interesting hypothesis that deserves to be further tested is that the uraninite appears to act as an intermediate storage for oxygen atoms (Section 2.4). Observations indicate that uraninite can become slightly oxidised and later release excessive oxygen, for example as uranyl ions.

6.3 CLAY BUFFER MATERIAL

6.3.1 Bentonite as a Barrier

The function of the buffer material is to: a) constitute a mechanical and chemical zone of protection around the canister, b) limit the inward percolation of potentially corrosive substances from the groundwater to the canister surface, c) filter fine particulate and colloidal material that may form during canister reactions, and d) in the event of canister

corrosion, to limit the dispersion of leached radionuclides from the canister out into the bedrock. Other important physical properties of bentonite are a reasonable load-bearing capacity to support the weight of the waste package and an adequate thermal conductivity to dissipate heat generated by the waste. Natural analogues have played a major role in demonstrating the long-term stability of bentonite as a major barrier to waste package failure and ultimately radionuclide transport.

The properties of bentonite are determined by the interaction between water and the smectite component, usually montmorillonite. The mineralogical stability of the montmorillonite has been extensively studied in natural geological systems and the most common alteration product is illite, a clay showing markedly inferior physical properties in the context of a repository buffer material.

The Cigar Lake uranium occurrence, intimately associated with massive clays dominantly comprising illite, therefore offered the opportunity to study at first hand the role of illite (i.e. the worst case repository buffer scenario) in helping to shield the uranium orebody from water-rock interaction and eventual removal since its formation 1.3 Ga ago. Such information could provide valuable input data of buffer material properties to future repository performance assessments.

6.3.2   Relevance of Cigar Lake

Chemical and physical characterisation of the Cigar Lake core material shows the clay as representing a "worst possible repository case" of smectite to illite alteration with respect to crystal size, basal spacing and mineral-water interaction, although it should be pointed out that there is no evidence at Cigar Lake that the original clay material was indeed smectite. Theoretical calculations (Section 2.3), however, point to the formation of smectite and/or illite/smectite mixed layer phases during hydrothermal alteration of the host sandstones.

Assuming the conversion of smectite in the MX-80 reference clay to a clay form exemplified by the Cigar Lake material, changes in physical properties show:

* a decreased swelling pressure by at least one order of magnitude,

* an increased hydraulic conductivity by at least three orders of magnitude,

* a loss of expandibility and self-healing potential, and

* an increased stiffness and brittleness.

In the context of repository performance assessment, this marked deterioration of bentonite would not only seriously threaten the integrity of the bentonite buffer itself, but ultimately the long-term stability of the canister and waste form. However two points should be considered at this juncture; first, current performance assessment buffer material alteration models show the unlikelihood that bentonite will undergo major alteration during repository timescales to the extent represented to-day at Cigar Lake, and second, despite the very poor buffer qualities measured from the Cigar Lake material, in practice, the massive clay (i.e. illite):

* has provided an effective, long-term sealing of the uranium orebody (i.e. during the 1.3 Ga since ore formation),

* is stable under suitable conditions over geological timescales, and

* is an efficient barrier to radionuclide and colloid migration.

In summary, studies at Cigar Lake have shown that the clays, whilst exhibiting inferior physical qualities to the bentonite types considered for repository disposal, have provided an efficient sealant to groundwater flow and also to radionuclide dissolution and migration over repository timescales. *Physically*, this is demonstrated by the: 1) large difference in hydraulic conductivity (Winberg and Stevenson, 1994), and 2) the calculations and observations of radionuclide mass transport in the near-field of the orebody summarised by Liu et al. (1994). *Chemically*, the buffering capacity has been greatly facilitated by prevailing reducing groundwater conditions. Therefore, as long as the chemistry of the groundwaters is sufficiently reducing, a deterioration of the clay buffer material need not result in widespread radionuclide migration.

6.4   FINAL COMMENT

This Cigar Lake exercise has underlined the advantages of reviewing and reappraising existing analogue data when the dust has settled. Three important areas to repository assessment have been addressed and considerable progress has been made since the initial interpretation of the data. The other aspect that came to light was the need to pursue certain lines of interest which require limited additional field and/or analytical data. Time and resources should be available for this to be realised, and every completed analogue study should retain some degree of *on-site* infrastructure to facilitate this possibility.

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7. ACKNOWLEDGEMENTS

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