GEOMETALLURGY AND PROCESSING OF AUSTRALIA’S URANIUM DEPOSITS

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ABSTRACT

Key issues confronting the Australian uranium mining industry include: the prevalence of low grade ores; a lack of detailed chemical and mineralogical information for the various ore deposit types; the presence of refractory uranium-bearing minerals and high acid-consuming gangue minerals, and; complex processing flowsheets.

CSIRO has sought to address the problem of the lack of chemical and mineralogical information by initiating a characterisation project focusing on the generation of detailed chemical and mineralogical data from a range of Australian uranium deposits. These include examples from iron ore-copper-gold-uranium (IOCU), metasomatite, surficial, unconformity-related, sandstone-hosted and vein-type uranium deposits. For representative samples from each deposit, the abundance and type of uranium minerals and associated gangue minerals were determined using a combination of techniques including X-ray fluorescence spectroscopy, X-ray diffraction, automated reflectance spectroscopy (HyLogging™) and high resolution electron probe microanalysis (EPMA).

Future work aims to use the insights gained through analysis of the chemistry and mineralogy of different ore types to assist industry in developing new and improved processing routes for these so-called ‘challenging’ uranium deposits.
INTRODUCTION

Australia has about 38% of the world’s uranium resources and uranium is a major export earner for the country generating about $1B annually. Major resources include the Olympic Dam iron-oxide copper-uranium-gold deposit (South Australia), the Ranger, Jabiluka, Koongarra (Northern Territory) and Kintyre (Western Australia) unconformity-related deposits, the Yeelirrie surface-related deposits (Western Australia) and the Beverley, Four Mile and Honeymoon sandstone-hosted deposits (South Australia). Australia is the third largest uranium producer in the world after Kazakhstan and Canada, however, uranium demand is forecast to grow significantly over the coming decades.

At present there are approximately 200 companies active in uranium exploration and project development in Australia. To assist these companies in developing and growing potentially new resources CSIRO, in collaboration with ANSTO and Geoscience Australia, recently generated a database containing information on more than one hundred Australian uranium deposits and advanced occurrences\(^1\). The work highlighted many of the key challenges that Australia’s uranium industry faces, including: low grade ores, complex deposit types, a lack of detailed mineralogical information on the main uranium and gangue minerals, the common occurrence of refractory uranium-bearing minerals (e.g. brannerite, and davidite) in the main ore types, the presence of high acid-consuming gangue minerals, and complex processing flowsheets.

Based on the information collected during construction of the database, two major recommendations were made:

1. Detailed ore characterisation information including chemical, mineralogical and textural data is required for many deposits, and,

2. Further metallurgical testwork is required to fill in process performance data.

CSIRO has sought to address the first recommendation by initiating a characterisation project which focuses on the generation of detailed chemical and mineralogical data from a range of Australian uranium deposit types. These included examples from iron ore-copper-gold-uranium (IOCGU), metasomatic, unconformity-related, vein, surficial, and sandstone uranium deposits. The aim of the project is to deliver new processing technologies to grow the Australian uranium ore reserve inventory, by linking geology and materials characterisation to metallurgical process solutions through the characterisation of a range of sample from sub-economic and problematic uranium resources using a number of routine and advanced elemental and mineralogical analytical techniques including; X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), automated reflectance spectroscopy (HyLogging\(^\text{TM}\)), automated mineralogical analysis (QEMScan) and high resolution electron probe microanalysis (EPMA).

In this paper, recent progress made in the characterisation of materials from low-grade, complex multi-metal and refractory deposits is discussed. Future work aims to use the insights gained through analysis of the chemistry and mineralogy of different ore types to assist industry in developing new and improved processing routes for these so-called ‘challenging’ uranium deposits.

SAMPLES

In order to gain access to samples from as diverse a range of deposits as possible, CSIRO solicited samples from companies who operate, develop or explore uranium deposits in Australia. The focus was centred on companies who required detailed characterisation testwork information from low-grade and/or metallurgically challenging deposits. A detailed report on the findings was provided on completion.

In total, thirty-nine samples representing at least six different deposit types were examined. These included:
• **IOCGU Deposits** (9 samples)
• **Unconformity-related Deposits** (4 samples)
• **Vein Deposits** (10 samples)
• **Surficial (Calcrete-hosted) Deposits** (6 samples)
• **Sandstone Deposits, including Lignite-hosted sandstone/clay deposits** (7 samples)
• **Metasomatite Deposits** (3 samples)

**RESULTS AND DISCUSSION**

Analysis of the chemical and mineralogical characterisation results from the six deposit types examined highlighted that the three mineralisation types; lignite-hosted sandstone, surficial and metasomatite, presented unique and challenging characterisation and processing problems. The characterisation problems were associated with the ability of available analytical techniques such as XRD, QEMScan and EPMA to locate the source(s) of the uranium in the deposit, particularly at the low levels present (e.g. most surficial deposits had uranium contents in the range 60-560 ppm U) and the fine grainsize of the uranium phase. In addition, the ability to adequately characterise and quantify the abundance of potentially problematic gangue phases such as swelling clays (e.g. the smectite group of clays) or acid-consuming gangue (e.g. calcite, dolomite) was important as these potentially can severely impact processing economics. In the following sections, the main features of each of these three deposit types are described, a summary of some of the characterisation results obtained is provided as well as a brief discussion of potential processing options. Note that results from the remaining three uranium deposit types; IOCGU, sandstone, and unconformity-related, also offered some challenging characterisation issues (e.g. extremely fine, sub-micron grainsize, particularly in the IOCGU ores), however in general, the processing of these ores is usually considered more straightforward. Results from these deposit types are not discussed in this paper.

**Calcrete-hosted surficial uranium ores**

In Western Australia, extensive surface or near surface calcrete-hosted uranium deposits occur largely in the Yilgarn Block where the deposits are found in Tertiary to Quaternary aged channels which drain the uranium-rich Archaean granitoids and greenstone basement\(^{(5)}\). Due to differences in environmental characteristics such as soil type, groundwater chemistry and climate, the calcrete deposits are confined to the northern portion of the Yilgarn Block in a broad region extending from Meekatharra in the northwest to Leonora in the southeast (Fig. 1). Within this region, calcrete-hosted deposits comprise 3-4% of known uranium resources in Australia, ranked fourth after IOCGU (74%), unconformity-related (17%) and sandstone-hosted (4%) ore types\(^{(5)}\).

While calcrete-hosted deposits represent only a small percentage of Australia’s uranium resources, they are the dominant deposit type in Western Australia where they make up ~65% of all known WA deposits. They tend to be medium to large tonnage deposits but of low grade. For example, the world’s highest grade calcrete-hosted deposit is the Yeelirrie deposit which contains 44,100 tonnes of uranium ore at an average grade of 0.13% U\(^{3+}\). Other significant prospects in WA include Lake Maitland, Wiluna (Lake Way and Centipede), Hillview and Thatcher Soak. The uranium grade of the northern Yilgarn calcrete-hosted deposits typically varies from 75 ppm to 1,500 ppm U\(_2\)O\(_6\). The uranium mineralisation is usually the mineral carnotite, a potassium-uranium-vanadium oxide with the chemical formula K\((UO_2)_2(VO_4)_2\cdot 3H_2O\), comprising 59.86% UO\(_2\)^{(5,6)}.
In addition to the well known calcrete-hosted deposits of the Yilgarn region, uranium deposits are also known to occur in Tertiary calcrete overlying Proterozoic granite and metamorphics of the Gascoyne Province of northwest Western Australia\(^4\). The deposits occur in a cluster approximately 200-250 east northeast of Carnarvon and include deposits such as Minindi Creek-Wabli Creek, Jailor Bore, Lamil Hills, Munaballya Well South, and Red Hill Well (Fig. 1).

Figure 1: Location of major calcrete-type uranium occurrences in the Yilgarn and Gascoyne districts, Western Australia (modified from Aral \textit{et al}\(^7\)).

CSIRO has analysed samples from two deposits in the northern Yilgarn and two deposits in the Gascoyne Province. For each deposit, the samples were examined by combined X-ray diffraction (XRD) X-ray Fluorescence (XRF) spectroscopy and electron microprobe (EPMA) techniques. Results from the XRF and XRD examinations are provided in Table 1.
Table 1: Mineralogical and chemical data for pairs of samples collected from two different northern Yilgarn and two different Gascoyne province calcrete uranium prospects.

<table>
<thead>
<tr>
<th>Prospect</th>
<th>Mineralogy (listed in approx. order of abundance)</th>
<th>U (ppm)</th>
<th>V₂O₅ (ppm)</th>
<th>K₂O (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>Al₂O₃ (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Northern Yilgarn</strong></td>
<td></td>
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<tr>
<td>NY1a</td>
<td>Quartz, Dolomite, Montmorillonite (Illite), Kaolinite, Albite, Muscovite, Halite</td>
<td>496</td>
<td>310</td>
<td>0.449</td>
<td>18.9</td>
<td>17.60</td>
<td>23.4</td>
<td>1.18</td>
<td>2.16</td>
<td>0.173</td>
</tr>
<tr>
<td>NY1b</td>
<td>Quartz, Dolomite, Calcite, Kaolinite, Albite, Muscovite, Halite, Hematite</td>
<td>562</td>
<td>530</td>
<td>1.14</td>
<td>8.13</td>
<td>9.24</td>
<td>48.1</td>
<td>3.68</td>
<td>6.91</td>
<td>0.256</td>
</tr>
<tr>
<td>NY2a</td>
<td>Quartz, Calcite, Kaolinite, Muscovite, Halite, Hematite</td>
<td>62</td>
<td>70</td>
<td>0.54</td>
<td>16.0</td>
<td>3.60</td>
<td>52.6</td>
<td>1.57</td>
<td>4.99</td>
<td>0.043</td>
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<tr>
<td>NY2b</td>
<td>Quartz, Calcite, Kaolinite, Halite, Hematite</td>
<td>81</td>
<td>&lt;DL</td>
<td>0.278</td>
<td>20.9</td>
<td>3.83</td>
<td>48.3</td>
<td>0.76</td>
<td>2.41</td>
<td>0.059</td>
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<tr>
<td><strong>Gascoyne Province</strong></td>
<td></td>
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<tr>
<td>G1</td>
<td>Quartz, Dolomite, Bassanite, Muscovite, Sanidine, Kaolinite, Albite, Palygorskite</td>
<td>409</td>
<td>410</td>
<td>1.80</td>
<td>18.7</td>
<td>12.1</td>
<td>24.2</td>
<td>3.2</td>
<td>4.51</td>
<td>2.11</td>
</tr>
<tr>
<td>G2</td>
<td>Quartz, Dolomite, Sanidine, Palygorskite, Muscovite, Kaolinite, Albite</td>
<td>394</td>
<td>270</td>
<td>1.67</td>
<td>19.4</td>
<td>13.0</td>
<td>26.9</td>
<td>2.3</td>
<td>3.94</td>
<td>0.040</td>
</tr>
</tbody>
</table>

The uranium grades of the four northern Yilgarn samples in Table 1 vary from 60-560 ppm U, which in general, represents the extremes in grade variations of the calcrete-hosted ores in the northern Yilgarn (except for the highly anomalous Yeelirrie deposit). The vanadium content also varies accordingly and ranges from 70-530 ppm V₂O₅. The high vanadium content in samples NY1a and NY1b is consistent with the likely presence of the uranium-bearing carnotite. Three of the four samples represent the carbonate-rich section of the calcrete (NY1a, NY2a and NY2b) giving rise to high levels of CaO and, in the case of sample NY1a, high MgO. It is noted that sample NY1a contains dolomite as the primary carbonate mineral whereas samples NY2a and NY2b contain calcite. The remaining sample, NY1b, is an example of ore from the ‘earthy’ section of the calcrete deposit, close to the transition between the calcrete and the underlying clay-quartz. This is reflected by the high SiO₂, Fe₂O₃ and Al₂O₃ contents giving rise to minor amounts of aluminosilicates and Fe-oxide in the mineral assemblage.
The uranium grades in the two Gascoyne Province samples are both around 400 ppm while the vanadium content ranges from 270-410 ppm $V_2O_5$. Quartz and dolomite are the main gangue minerals in both samples although sample G1 also contains a minor amount of bassanite (2CaSO$_4$·[H$_2$O]). The presence of bassanite is also reflected in the significantly higher S levels recorded for this sample compared to all other calcrete-hosted samples in Table 1. The presence of palygorskite (a clay weathering product after feldspar), is a swelling-type clay which may potentially cause problems during beneficiation.

A representative image resulting from the EPMA mapping is shown in Figure 2 for sample NY1a. The mapping confirmed that the main uranium bearing mineral in this deposit (and also the others) was carnotite. Although the carnotite in Figure 2 appears reasonably coarse-grained, high resolution imaging using a scanning electron microscope indicates the carnotite-rich regions are made up of numerous small particles of carnotite crystals (Figure 3). This texture was also present in the other calcrete samples examined and is consistent with a mode of formation whereby the carnotite is precipitated out of solution.

Figure 2: Mineral phase maps for sample NY1a showing the disseminated nature of the carnotite (white). Data was collected using a JEOL 8500F EPMA equipped with five wavelength dispersive spectrometers and two solid-state energy dispersive detectors (after Aral et al[7]).

Based on the characterisation results from the six samples the key findings are as follows:

- All deposits examined contained carnotite (hydrated potassium uranium vanadium oxide) as the only U-bearing mineral. The carnotite was typically fine-grained (sub-micron to 10 µm across, and only occasionally up to 20 µm) and occurs as inclusions in carbonates and/or clays (Figure 2), and rarely occurred as fully liberated grains which makes beneficiation by physical means difficult, if not impossible.

- Depending on the deposit, the gangue mineralogy is dominated by carbonate (dolomite, [Ca,Mg]CO$_3$, or calcite, CaCO$_3$), quartz (SiO$_2$), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), albite (NaAlSi$_3$O$_8$), feldspars (KAlSi$_3$O$_8$), muscovite (KAl$_2$[AlSi$_3$O$_10$][OH]$_2$), swelling
clays e.g., smectite, montmorillonite, palygorskite ([Mg,Al]_2Si_4O_{10}(OH)·4(H_2O)), clinohore ([Mg,Al]_3Si_5O_{10}(OH)_6), halite (NaCl), gypsum (CaSO_4), bassanite (2CaSO_4·H_2O) and Fe-oxides. Calcite, gypsum, dolomite, ferric oxide, and halite are the typical cementing minerals.

- From a processing point of view, the high carbonate content indicates an acid leach process is unlikely to be economically feasible and therefore an alkaline leach route is required.

**Figure 3:** Back-scattered electron images of sample Y1 showing typical fine-grained textures of carnotite grains in calcrete ores. Image (a) shows small carnotite grains (bright phase) as inclusions in dolomite while images (b) and (c) show high mag. views of carnotite grains. Dol = dolomite, Qtz = quartz and Ct = carnotite (after Aral et al.

**Processing options for calcrete-hosted surficial uranium ores**

The mineralogy of the calcrete ore, in particular the gangue constituents and other minerals present, exerts the greatest influence over process selection. The chemical nature of the ore determines the type of treatment employed and, since the calcrete-hosted deposits contain significant quantities of calcium (as calcite, dolomite or in some cases gypsum), a process using an alkaline carbonate-based lixiviant is the preferred option. Acid leaching is generally not a viable option for these ores as the carbonate minerals will consume an excessive amount of acid. Alkaline leaching also has several other advantages over acid leaching. These include: (a) the inherent selectivity of the alkaline solution for uranium, (b) its noncorrosive nature on typical materials of construction, and (c) the relative ease of recovering the uranium from solution and regenerating the leach liquor.

Carbonate-containing uranium ores containing approximately 1000 ppm or more uranium are traditionally leached with a sodium carbonate-sodium bicarbonate mixture in tanks at 80-90°C or in autoclaves around 120°C (6). However, when the ore grade is less than typically 500 ppm U, the economic viability of the alkaline tank/autoclave leach routes become
questionable. The low grade of calcrete-hosted uranium deposits and their occurrence close to the surface make them potential candidates for heap leaching.

Although the uranium industry recognises that heap leaching of calcrete-hosted uranium ores could play an important role in their processing, the technology needs to be better understood before it can be applied. The two main issues that require clear understanding are as follows:

- Inconsistent and unpredictable rate of extraction influenced primarily by the initial rate of reaction. In other words, the conditions that effectively initiate the reaction are not well understood.
- An inability to increase the uranium tenor of recycled pregnant liquor solution beyond a limiting concentration. As well as having severe economic implications this highlights the fact that side reactions (loss of uranium by precipitation and/or adsorption on gangue minerals) could be occurring within the heap that are not at all understood.

Uranium leaching using alkali carbonates is sensitive to a variety of factors including: the mineral surface area and particle size, agitation, pulp density, oxygen partial pressure, temperature, sodium carbonate and bicarbonate concentration, pH and Eh. In a heap leach important factors also include the heap permeability, the presence of carbonate consuming gangue minerals, and adsorption of uranium from the pregnant leach solution onto gangue minerals.

The presence of swelling type clays such as smectite, montmorillonite, saponite and palygorskite is also a problem in heap leaching as it could cause channeling and reduced permeability. The Western Australian calcrete-hosted uranium ores can contain 15-20% montmorillonite (swelling type clay) accompanied with dolomite and/or calcite (up to 60-70%) and 5% quartz. There are reports suggesting a strong, inverse relationship between the calcite content and the swelling rate of the clay\(^9\).

**Metasomatite deposits**

Less than 2% of Australia’s uranium resources are in this type of deposit\(^{10}\). Metasomatite deposits occur in the Eastern Creek Volcanics north of Mount Isa, Queensland where there are more than one hundred small uranium deposits and prospects of this type, the largest of them being Valhalla, Skal, Bikini and Anderson’s Lode (Figure 4). The deposits typically consist of unevenly disseminated uranium in structurally deformed rocks that were affected by sodium metasomatism. Metasomatic host rocks include albities, and alkali amphibole rocks. The principal ore minerals in metasomatite deposits are U-rich oxides and silicates, including uraninite, coffinite, U-Ti oxide minerals (including brannerite) and U-rich zircon. The latter minerals are refractory and are difficult to beneficiate using conventional acid-leach processes.

The host rocks in metasomatite deposits usually show several types of alteration. Typically the rocks show sodium-metasomatism which results in enrichment in \(\text{Na}_2\text{O}\) and depletion of \(\text{SiO}_2\). Hematite and carbonate alteration is usually present. Albirites that host the mineralisation often occur along mylonitic zones or major fault zones.

Ore grades in metasomatite deposits are low, usually less than 0.2% \(\text{U}_3\text{O}_8\), but may range up to 3% \(\text{U}_3\text{O}_8\). A composite sample from a Valhalla drill cores examined by Goldney \textit{et al.}\(^{11}\) contained on average 0.16%, \(\text{U}_3\text{O}_8\) in brannerite and metamict zircon. The metamict zircon grains contained approximately 8% \(\text{U}_3\text{O}_8\). The major gangue minerals identified in the mineralised zone were albite, dolomite (~20.9% \(\text{CaCO}_3\) equivalent), quartz, sodic pyroxene, and sodic amphibole. The proportions of these minerals vary considerably throughout the mineralized zone.

CSIRO has analysed samples from two metasomatite deposits in the Mt Isa region. Results from the XRF and XRD examinations are provided in Table 2.
Figure 4: Regional geology of the Mount Isa Inlier and principal uranium deposits and prospects (after McKay and Miezitis).

Table 2: Mineralogical and chemical data for samples collected from two different Mt Isa region metasomatite uranium prospects.

<table>
<thead>
<tr>
<th>Prospect</th>
<th>Mineralogy (listed in approx. order of abundance)</th>
<th>U (ppm)</th>
<th>TiO₂ (%)</th>
<th>Na₂O (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Th (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI-1</td>
<td>Albite, Dolomite, Quartz, Clinochlore, Muscovite, Calcite, Magnetite</td>
<td>3010</td>
<td>1.86</td>
<td>5.09</td>
<td>8.39</td>
<td>6.02</td>
<td>44.0</td>
<td>9.50</td>
<td>10.5</td>
<td>29</td>
</tr>
<tr>
<td>MI-2</td>
<td>Albite, Dolomite, Quartz, Calcite, Riebeckite, Magnetite, Hematite, Clinochlore</td>
<td>3890</td>
<td>2.29</td>
<td>4.56</td>
<td>8.65</td>
<td>3.83</td>
<td>44.0</td>
<td>13.8</td>
<td>8.66</td>
<td>87</td>
</tr>
</tbody>
</table>
The XRF results indicate a slightly higher level of uranium in the MI-2 sample (0.39 wt. % U) compared to MI-1 (0.3 wt. % U) and both samples contain high sodium, aluminium and silicon levels consistent with albitisation of the host rocks. The XRD analysis of the two samples showed the mineralogy is dominated by the presence of albite, dolomite and quartz. Calcite and magnetite are present in both samples; however, there appears to be proportionately more of each in the MI-2 sample. The MI-1 sample also contains significantly more clinohlore than the MI-2 sample. Minor minerals present at levels of less than ~2% were not detectable by XRD.

EPMA mapping of the two Mt Isa metasomatite samples did not indicate any significant differences in mineralogy between the two samples. Two mapped regions showing the main mineral phases and textures observed in the MI-V1 sample are shown in Figure 5. Both samples were dominated by the mineral assemblage albite, dolomite and quartz with minor magnetite, calcite, K-rich feldspar, chlorite, rutile, apatite and muscovite and trace amounts of U-containing zircon, riebeckite and galena. The main mineral assemblage in both samples was in good agreement with that determined using XRD.

Figure 5: The occurrence of coffinite and brannerite in a dolomite-hosted uranium ore from Mt Isa region of Queensland.

The uranium minerals identified by EPMA were brannerite and coffinite. Brannerite appeared to be the main U-bearing mineral in sample MI-2 and was present in late veinlets (post albitisation) that were characterised by the assemblage quartz+K-feldspar+rutile±chlorite±ilmenite. Sample MI-1 also contained brannerite; however, coffinite was common throughout the sample. Coffinite appears much lower in abundance and tends to be associated more with the host-rock mineral assemblage of quartz+albite+dolomite±calcite±magnetite. The coffinite does not appear to be associated...
with the later vein-filling brannerite-rich assemblage. Uranium is also present, in minor amounts, within zircon grains.

**Processing options for metasomatite uranium ore deposits**

The occurrence of brannerite in association with acid consuming gangue minerals such as dolomite and calcite creates the greatest challenge in defining a cost-competitive flowsheet for the treatment of metasomatite ores. Brannerite ores are known to require stronger leaching conditions than ores containing uraninite or secondary uranium minerals\(^8\)\(^{11}\). Goldney *et al.*\(^{11}\) showed, using a brannerite-rich ore from the Valhalla prospect, that over 80% extraction of uranium could be obtained with sulphuric acid leaching at 50ºC with continuous agitation over a period of 50 hours, provided the ore was finely ground to –63 microns and the free acidity of the leach liquor was maintained at 0.5N or higher throughout the leaching period. Similar results could be achieved in shorter times using higher free acidity levels and/or higher temperatures.

The addition of oxidant, either as MnO\(_2\) or as a soluble ferric salt increased the rate of leaching significantly under most conditions and also increased the final leaching efficiency. The effect of the addition of oxidant was more significant at the lower free acidity levels. Finer grinding of the ore to –45 microns resulted in a small improvement in leaching rate and in final extraction in tests at 50ºC, but had no effect in tests at 70ºC. Goldney *et al.*\(^{11}\) therefore concluded that finer grinding would not be worthwhile, and in fact the optimum grind size could well be coarser than the -63 microns size used in their tests.

Goldney *et al.*\(^{11}\) also concluded that the need to maintain a relatively high free acid concentration would call for a two stage counter-current leaching system with intermediate solids separation. The free acid remaining in the leach liquor at the end of the main leach would thus be neutralised by the carbonate content of the ore in the fresh ore leaching stage. They also emphasised the need for a substantial separation of dolomite from uranium minerals before leaching, as the major processing problem remains one of reducing acid consumption. Goldney *et al.*\(^{10}\) showed effective separation of dolomite from uranium minerals by sizing, gravity separation, or magnetic separation was not possible. However, froth flotation of dolomite and calcite was successful to some extent and as a result the carbonate levels could be reduced from ~21% to as 7% CaCO\(_3\) equivalent. The amount of uranium upgrading as a result of flotation was small.

Mineralogical testwork on Valhalla ore by Henley *et al.*\(^{12}\) suggested that liberation of the brannerite from the gangue would require very fine grinding and physical beneficiation. They concluded however that this would probably not be effective in upgrading the uranium content of the ore without unacceptable losses of uranium in tailings. This was based on density gradient separation results conducted on two size fractions of Valhalla ore (–710 +250 µm and –180 +63 µm) which showed that there is virtually no preferential grinding of the brannerite (calculated assays of size fractions are similar) and there is less than 5% liberation of uranium in the two size fractions, the uranium being distributed throughout the density range.

The effectiveness of an alternative option that of alkaline leaching was also briefly investigated by Goldney *et al.*\(^{11}\). This resulted in a uranium extraction of 24% on a composite sample ground to –45 microns and leached at 50ºC for 50 h using 50g Na\(_2\)CO\(_3\) and 50g NaHCO\(_3\). A similar leach at 20ºC resulted in 18% extraction of uranium while an alkaline leach at 100ºC on a random Valhalla sample was ineffective\(^{11}\).

Based on the limited amount of work conducted so far on the Mt Isa region metasomatite ores, the successful processing of brannerite-containing ores will be difficult to achieve unless acid consumption by carbonates can be reduced significantly. It is recommended that more detailed studies of both physical beneficiation and chemical processing of metasomatites ores will be required if commercial development of the deposits are considered.
Lignite-hosted uranium ores

Uranium in Western Australia (WA) also occurs in surficial lignite-hosted deposits and the CSIRO database includes XRD, XRF and EPMA results from some of these ores (e.g. Mulga Rock deposit and Junction prospect). These lignite-hosted deposits northeast of Kalgoorlie (WA) are uranium-bearing, polymetallic mineral deposits; found in association with palaeochannel sediment sequences (e.g. Figure 6). At Mulga Rocks, the deposit comprises three separate zones of mineralisation – Shogun, Emperor and Ambassador deposits. These occur along the outer margin of a broad bend in the palaeochannel. The uranium mineralisation is hosted by peat and clayey peat and occurs immediately below the redox boundary at the base of the weathered zone\(^\text{(2)}\). The mineralized zones are flat-lying, approximately 20-50 m below surface, and average about 2m in thickness. Uranium minerals are generally not present, although rare coffinite and uraninite have been observed\(^\text{(2)}\), and it is believed that uranium has been adsorbed onto the organic matter within the peat\(^\text{(13)}\).

![Figure 6: Location of the two lignite-hosted uranium deposits examined in this study.](image)

The samples from lignite-hosted deposits are typically dark brown to black coloured, soft, friable materials (Figure 7). Uranium grades are generally very low and average less than 0.001% \(\text{U}_3\text{O}_8\) in typical lignite-hosted deposits\(^\text{(10)}\) although the Mulga Rocks deposit appears anomalous with an average of 0.12% \(\text{U}\)\(^\text{(13,14)}\).

CSIRO has analysed samples from two lignite-hosted deposits from WA. Results from the XRF and XRD examinations are provided in Table 3.
Figure 7: The general appearance of lignite-hosted uranium samples from Western Australia. Both samples are dark in colour and are typically friable when handled.

Table 3: Mineralogical and chemical data for samples collected from two different lignite-hosted uranium prospects.

<table>
<thead>
<tr>
<th>Prospect</th>
<th>Mineralogy† (listed in approx. order of abundance)</th>
<th>U (ppm)</th>
<th>TiO₂ (%)</th>
<th>K₂O (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>Al₂O₃ (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-1‡</td>
<td>Quartz, Kaolinite, Cu-Fe sulphides, Calcite, Rutile, Galena, Zircon, (Zn,Ni)O oxides and sulphides</td>
<td>1.37</td>
<td>0.33</td>
<td>0.09</td>
<td>0.75</td>
<td>0.53</td>
<td>13.3</td>
<td>0.89</td>
<td>11.3</td>
<td>0.144</td>
</tr>
<tr>
<td>L-2</td>
<td>Quartz, Illite, Kaolinite, Orthoclase, Chlorite, Pyrite</td>
<td>93</td>
<td>0.56</td>
<td>1.76</td>
<td>0.63</td>
<td>1.09</td>
<td>55.8</td>
<td>5.44</td>
<td>20.3</td>
<td>1.04*</td>
</tr>
</tbody>
</table>

† Note that amorphous, carbonaceous material is not observable by XRD.
‡ Sample L-1 also contains significant levels of other metals including 0.61% PbO, 0.29% NiO, and 0.14% ZnO.
* determined via LECO analysis.

Attempts to locate uranium minerals in the carbonaceous ores were difficult. EPMA mapping conducted at 200 nm resolution failed to identify any unique uranium mineral in the samples. High resolution mapping for uranium indicated, however, a close association between uranium and carbon (Figure 8). Moreover, in one of the samples examined, two types of carbonaceous material were identified within the sample (Figure 9). The first type of lignite was a smooth textured, sulphur-rich carbon phase containing some uranium. The second type was characterised by having a more mottled texture and containing significant amounts
of S, Na, Al, Mg, Si, O and U impurities. It is likely that the Na, Mg, Al, Si and O within the carbon represents fine-grained, sub-micron sized aluminosilicate clays that are intimately mixed with the lignite but not resolvable as a separate phase using the EPMA. Results are consistent with the uranium being present as an adsorbed species on the surface of the carbonaceous material. Along with uranium, a number of other trace elements were strongly enriched in the lignite-hosted sample shown in Figure 9, particularly S and V, many transition metals (including sulphides of Co, Cu, Ni, Pb and Zn), rare earth elements and Y.

**Figure 8:** Uranium distribution map (Fig. 8a) plus a uranium and carbon distribution map (Fig. 8b) showing the correlation between carbon and uranium in a lignite-hosted sample. The scale bar in Fig. 8a represents relative concentration of uranium. The circular structures evident in the maps appear to be relict cellular material from carbonaceous matter.

An association of uranium with medium rank coaly carbonaceous materials that was observed in the Mulga Rock and Junction deposits has been frequently observed in other deposits with lignite often the most efficient host organics for U deposits\(^{(15,16,17)}\). Mohan *et al.*\(^{(18)}\) provided experimental evidence that indicates that uranium in a lignite from Karnes County, South Texas, occurs principally (70-90%) in the form of uranyl humates and the rest in the form of poorly crystallised mineral(s). Elsewhere, Eakin and Gize\(^{(19)}\) investigated uraniferous bitumens from Great Britain, Scandinavia and South Africa by oil-immersion reflected light microscopy and suggested that uraniferous bitumens were formed during complexation/reduction reactions. Meunier *et al.*\(^{(20)}\) pointed out the presence of a good correlation between uranium, total sulphur, and organic carbon. Uranium is mainly fixed in organics as organo-uranyl compounds. Uranium minerals detected include coffinite, pitchblende, and secondary hexavalent U minerals. According to these authors accumulation of uranium, aided by adsorption processes, was favoured by a permeable, organic-rich, and slightly acid environment. Uranium in lignites is also known to occur in Idaho, Wyoming, Montana, and North and South Dakota. The western Dakotas’ lignite deposits contain uranium in concentrations averaging 0.1 to 0.2 percent \(U_3O_8\).

A second possible U-fixing mechanism for the lignite-hosted uranium deposits is that of U adsorbed on the surfaces of sulphides. Wersin *et al.*\(^{(21)}\) studied the interaction of aqueous \(U^{(VI)}\) with galena and pyrite surfaces under anoxic conditions by solution analysis and by spectroscopic methods. They concluded that sulphide minerals are efficient scavengers of soluble uranyl complexes and that thermodynamically metastable \(U_3O_8\) controls uranium concentrations in many anoxic groundwaters.
Figure 9: The occurrence of uranium in association with a C, S, Al/Si/O phase (shown in red) in a lignite-hosted uranium ore from Western Australia.

Processing options for lignite-hosted uranium ores

Processing of lignite-hosted uranium ores using sulphuric acid for extracting uranium is possible but large amounts of acid would remain in the porous matrix of lignite/peat. As a result direct leaching would not utilise recyclable excess acid and generate large volumes of acidic solid waste. Acid leaching would also not make use of the calorific value of the host lignite. An alternative option is ashing/burning the lignite followed by leaching. This could be done in-situ or on the run-of-mine. Ashing would significantly reduce the volumes to be handled, generate heat, power and water, and possibly improve the overall process economics.

The ash could be then leached with different lixiviants, for example with sodium carbonate to selectively extract uranium, with cyanide to recover gold and sulphuric acid leach to extract Sc, Ni, Co and rare earth elements (REEs).

CONCLUSIONS

Detailed chemical and mineralogical data were obtained from a range of Australian uranium deposit types including; iron ore-copper-gold-uranium (IOCGU), metasomatic, unconformity-related, vein, surficial, and sandstone uranium deposits. Analysis of results from the six deposit types highlighted that the three mineralisation types; lignite-hosted sandstone,
surficial and metasomatite, presented unique and challenging characterisation and processing problems. The characterisation problems were associated with the ability of available analytical techniques such as XRD, QEMScan and EPMA to locate the source(s) of the uranium in the deposit and the frequently observed fine grainsize of the uranium phase(s). In addition, the ability to adequately characterise and quantify the abundance of potentially problematic gangue phases such as swelling clays or acid-consuming gangue (e.g. calcite, dolomite) was important as these potentially can severely impact processing economics.
REFERENCES


