

WATER AND CARBONATE BALANCES IN AN ALKALINE URANIUM EXTRACTION CIRCUIT

by

Mike Dry

Arithmetek Inc. Ontario, Canada

mike.dry@arithmetek.com

ABSTRACT

This paper presents the results of an exercise in which a generic alkaline circuit for uranium extraction was examined. The water and carbonate balances were analyzed, the objective being to minimize the overall consumption of sodium carbonate and sodium hydroxide in the circuit. The results of this exercise show that, for the circuit studied, the overall consumption of reagents is minimized when the amount of fresh water used as wash water in the solid-liquid separation section is balanced by the water remaining in and evaporated from the final consolidated tailings. More than that amount of fresh wash water results in an excess of barren solution from the ion exchange section. Using less than that amount of fresh wash water unnecessarily increases the amount of carbonate reporting to the tailings facility and therefore the amount of carbonate locked in the consolidated tailings.

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1. INTRODUCTION

Depending on the nature of any particular uranium ore, it is processed using either acid or alkaline hydrometallurgy. The individual unit operations in uranium hydrometallurgy have been proven commercially. This paper examines the extraction of uranium using sodium carbonate as the lixiviant. The focus is on the overall water and carbonate balances and the objective was to minimize the consumption of sodium carbonate and sodium hydroxide.

2. ORE

An ore containing hexavalent uranium was selected for this exercise, but a similar exercise could just as easily have been done for an ore containing pentavalent uranium, or for a circuit using acid as the lixiviant. Table 1 shows the input data used for this study. These numbers are loosely based on published information from the Langer Heinrich Uranium project in Namibia (1), merely to give some realism to this study.

Table 1 – Ore assays, parts per million

U ₃ O ₈ grade, mass %	0.06
Total ore reserve, Mt	51
Assumed leach extraction, %	99
Assumed life of mine, years	20
Calculated U ₃ O ₈ dissolution, tpa	1515

Table 2 is a calculated mineral assemblage representing the ore in Table 1. This representation is arbitrary and was assembled for the purposes of this study. In this example, the uranium mineral is carnotite and the clay minerals represent some of the more complex minerals one might expect to encounter in such ores. The calcium sulfate was included to provide sulfate, which consumes carbonate. The calcium carbonate was included to make alkaline leaching appropriate, rather than acid leaching. The bulk of the material is silica. Of course, any specific application would require information on the particular ore in question.

Table 2 – Representation of the ore, mass %

K ₂ (UO ₂) ₂ (VO ₄) ₂ •3H ₂ O	0.10
NaCa ₂ Fe ₄ Al ₃ Si ₆ O ₂₂ (OH) ₂	2
KAl ₃ Si ₃ O ₁₀ Cl ₂	3
CaSO ₄	0.5
CaCO ₃	10
SiO ₂	84.4

3. PROCESS CHEMISTRY

A generic alkaline uranium extraction circuit would contain the following process steps:

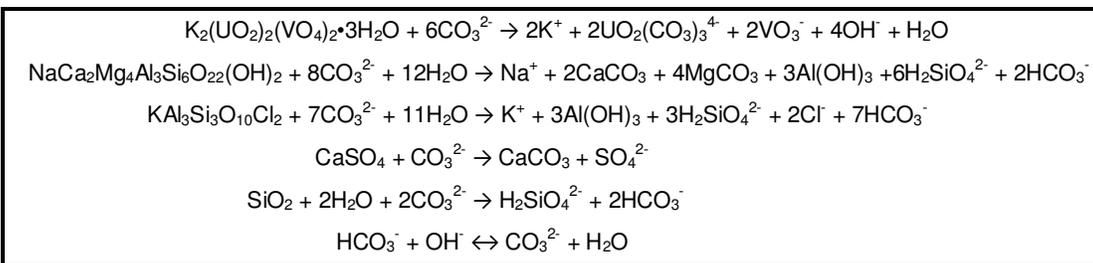
3.1. Ore preparation

It is sometimes possible to reject a significant portion of the ore as a barren waste, generating an upgraded feed to the circuit. In this exercise upgrading is ignored because it is case specific. In general, the feed to the leach section would be either run-of-mine or upgraded ore.

3.2. Leaching

The mineralogy of the ore largely dictates the chemistry of the leach. Table 3 shows stoichiometry used to represent the leaching of the ore in Table 2 in a solution containing sodium carbonate. The last equation is the carbonate-bicarbonate equilibrium that buffers the pH of the solution.

Table 3 – Leach stoichiometry



Allowing the pH to become too high, either from chemical reaction or from too high a carbonate concentration could cause some uranium to precipitate as sodium diuranate (see Table 6 below for the reaction concerned). To prevent this, a suitable level of sodium bicarbonate is generally maintained in solution to prevent the pH from rising excessively. The other reactions consume carbonate and generate bicarbonate, which is beneficial as long as the gangue dissolution does not consume excessive amounts of carbonate.

3.3. Solid-liquid separation

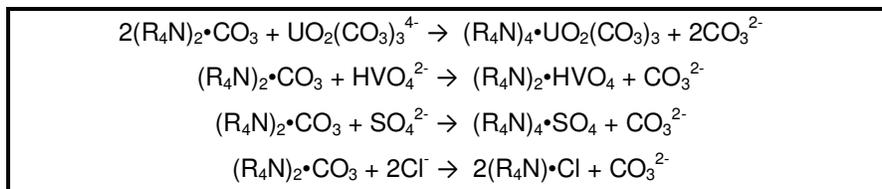
This could conceivably be done using filtration, but countercurrent decantation is often preferable. For this exercise, countercurrent decantation was assumed. In some cases resin-in-pulp technology is appropriate, in which case countercurrent decantation would be replaced by single-stage thickening. However the solid-liquid separation is done, it is necessary because the final solution has to be recycled to the leaching section to recycle carbonate.

3.4. Ion exchange

Strong base resins are used to extract the anionic uranium carbonate complex. Table 4 shows chemistry representing the extraction stage of the ion exchange sequence. The symbol (R₄N)⁺ represents the resin.

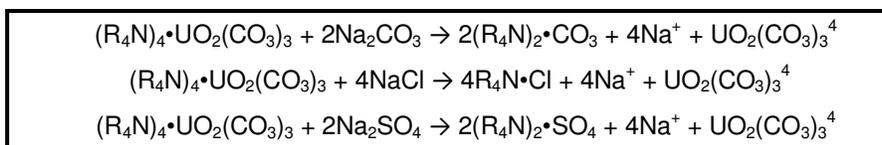
The extents to which species like vanadium, sulphate and chloride are co-extracted depend on the exact resin chosen and the exact process conditions.

Table 4 – Ion-exchange: extraction



Uranyl carbonate can be eluted from strong base resin by solutions containing 1 molar carbonate, bicarbonate, sulphate or chloride (2). Table 5 shows the relevant chemistry. The reactions for the elution of vanadium, sulphate and chloride with carbonate are the reverse of the loading reactions and those reactions for elution with sulphate, bicarbonate or chloride are analogous to the elution reactions using carbonate.

Table 5 – Ion exchange: elution

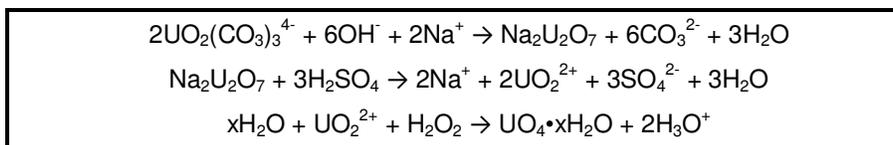


Combining the loading and elution reactions for uranium gives uranyl carbonate in the solution from the leach going to uranyl carbonate in the eluate and returns the resin to the extraction stage in its carbonate form. Elution with sodium carbonate would therefore appear to be a logical choice. Elution with chloride or sulfate might be appropriate in some circumstances, but that could require another step in which the resin is regenerated to the carbonate form before being returned to the extraction stage of the ion exchange sequence. In this exercise the ion exchange sequence was treated as a black box in which uranium is extracted completely and the vanadium, sulphate and chloride species are either not extracted or are extracted partially. For any specific application this would obviously need to be refined.

3.5. Precipitation and recovery

Typically, the eluate from ion exchange would contain uranium at the level of grams per liter. Adding sodium hydroxide to the eluate raises its pH and causes sodium diuranate (SDU) to precipitate. Table 6 shows the associated chemistry.

Table 6 – Precipitation and recovery of uranium



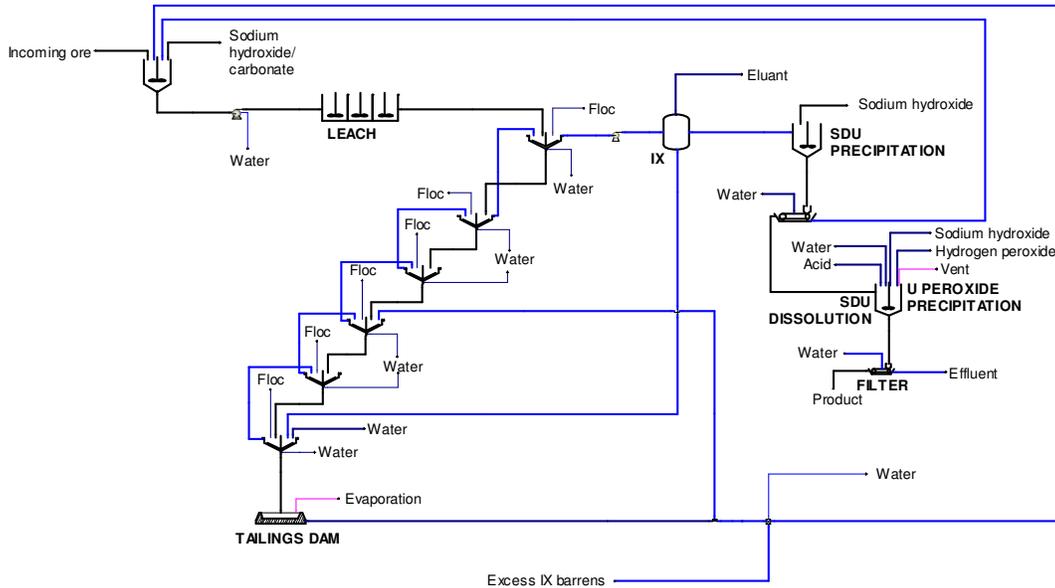
As uranium hydroxide is precipitated, some acid is released and is neutralized with sodium hydroxide. The SDU is separated from the solution, for example by filtration and washing with water. The washed SDU is then re-dissolved in sulfuric acid and water and hydrogen peroxide is

added to convert the dissolved uranium to precipitated uranium peroxide that is recovered, dried and packaged.

4. PROCESS MODEL

Figure 1 shows a generic uranium extraction circuit containing the sections described below.

Figure 1 – Generic uranium extraction circuit



4.1. Leach

Incoming ore is mixed with barren solution from the ion exchange section and high-pH solution from the precipitation of sodium diuranate. The leaching reactions shown in Table 3 occur. For this exercise the assumed extent of reaction is 99.5 percent for the dissolution of carnotite. The extent of dissolution of the clay minerals is such that the chemical consumption of sodium carbonate is 10, 20 or 30 kg per ton of solids leached. The calcium sulfate was assumed to convert completely to calcium carbonate and the quartz was assumed to be inert.

4.2. Solid-liquid separation

The leached slurry proceeds to a six-thickener countercurrent decantation train. Barren liquor from the ion exchange section is used as wash solution, entering at the fourth thickener and the final thickener in the train. Being depleted in uranium, the barren solution from ion exchange is suitable for the displacement of uranium from the leached slurry. However, not being depleted in carbonate, it is not able to displace carbonate from the slurry. For that reason, fresh water is also added to the final thickener in the train as a second wash solution. The objective of this configuration is to recover essentially all the uranium from the leached slurry and also to minimize the loss of carbonate to the final thickener underflow. This introduces a complication into the overall water balance, which is discussed further on.

The underflow leaving the final thickener goes to the tailings dam, where the solids consolidate further and release some solution from which water is partly lost to evaporation. The balance is

recovered as return dam water that joins the barren solution from the ion exchange section returning to the leach. The amount of water evaporated can be adjusted by adapting the design of the tailings dam if the operation is situated in a suitably arid region. The effect of the extent of the evaporation of water on the tailings dam is one of the items investigated in this exercise.

In reality, the overflow from the first thickener in the counter-current decantation train would pass through a filter or a clarifier. The simplified model used for this exercise assumes clear solution leaving the first thickener in the train.

4.3. Ion exchange

In reality the ion exchange section would include loading, elution and perhaps also regeneration and resin washing steps. For this exercise, all of that was initially taken as a black box in which sodium uranyl carbonate is transferred from the pregnant solution to the eluate leaving the ion exchange section and replaced with sodium carbonate from the eluant. In practice, the elution sequence would be arranged to achieve a desired concentration of uranium in the eluate. In this simplified model, the amount of the eluant was adjusted to give 10 g/L of U_3O_8 in the eluate.

This approach ignores the co-extraction of species like vanadium, sulfate and chloride. The engineering design of equipment for the ion exchange section would naturally require consideration of these species, but that detail was initially not part of this exercise. Any vanadium, sulfate or chloride loading onto the resin in the extraction stage would be eluted and returned to the leach in the solution leaving the precipitation of sodium diuranate, or if it precipitates with the sodium diuranate it would leave the circuit in the sodium sulfate effluent after the precipitation of uranium peroxide. Any of these species not loaded in ion exchange would return to the leach in the barren solution. Either way, these species are recycled to the leach, minus any part rejected with the sodium sulfate effluent. For this exercise, the exact recycle path is not important.

To check the effect of the extraction of species like vanadium sulfate and chloride, the model was modified to use the following resin selectivity ratios in the loading stage of the ion exchange section:

- Uranium over vanadium 100
- Uranium over sulfate 200
- Uranium over chloride 500

The selectivity ratio is defined as the amount of uranium on the resin over the amount of uranium in solution, divided by the amount of the other species on the resin over the amount of that species in solution. Because this exercise assumed complete elution of the resin, the amounts on the resin were approximated by the amounts in the eluate. For a “real” design, this would be refined.

4.4. Precipitation and recovery

The pH of the eluate from the ion exchange section is raised with sodium hydroxide, causing sodium diuranate to precipitate. In this model, enough sodium hydroxide is added to leave a residual of 10 g/L of NaOH after complete precipitation of the uranium. The resulting slurry is filtered and the filter cake is washed with water. The combined filtrate returns to the leach section

to recycle the carbonate and hydroxide. The washed filter cake is re-dissolved in sulfuric acid and water, then hydrogen peroxide is added to oxidize and precipitate the uranium. Excess hydrogen peroxide is used to ensure complete precipitation of the uranium. Any hydrogen peroxide not used for the oxidation of uranium was assumed to decompose to oxygen and water, the oxygen being vented. The resulting slurry is filtered and the filter cake is washed with water. The filtrate leaves the circuit as an effluent containing dissolved sodium sulfate. The washed filter cake leaves the circuit as the uranium product. In practice it would be dried and packaged for sale.

5. CARBONATE AND WATER BALANCE

Water enters the circuit at two main points - the incoming ore and the fresh water going to the final thickener in the countercurrent decantation train¹. Returning all the barren solution from the ion exchange section to either the countercurrent decantation train or to the leach section and also adding enough fresh water to the countercurrent decantation train to displace all the carbonate bearing solution would cause a water imbalance across the circuit. If the amount of water leaving in the underflow from the final thickener in the countercurrent decantation train balances the amount of fresh water added to the final thickener, and no other water enters the circuit, neglecting any water formed or consumed by chemical reaction, the water balance closes. In this ideal case, the ratio of fresh water to water in the washed underflow leaving the countercurrent decantation train would be unity, which would allow for a high displacement of carbonate from the slurry (complete displacement, given enough thickeners). However, the incoming ore does contain water, which means that the amount of fresh water that can be added without violating the overall water balance is less than the amount removed in the final underflow from countercurrent decantation. The return dam water and water introduced as gland seal water and flocculent additions further reduce the amount of fresh water that can be added as wash to the final thickener in countercurrent decantation if the overall water balance has to be maintained. Because of that, it is impossible for the fresh water added to the final thickener to displace all of the carbonate in the solution entering the countercurrent decantation train, simply because the wash ratio based on the fresh water is less than unity. If more fresh water is added than water is removed in the final consolidated tailings, not all of the barren solution from the ion exchange section can be recycled. The excess barren liquor constitutes an unnecessary bleed from the circuit, removing carbonate. Any carbonate lost from the circuit needs to be replaced with fresh carbonate.

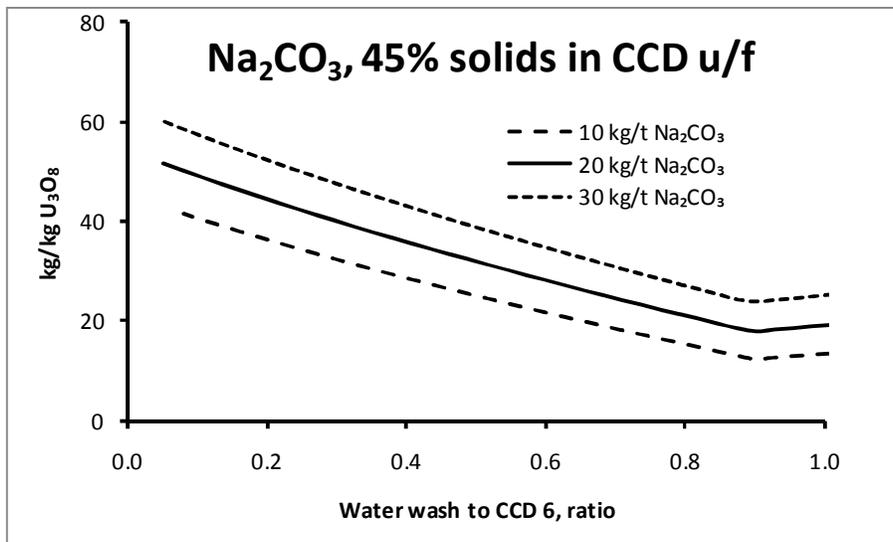
The consumption of carbonate in the leach is, of course, determined by the characteristics of the ore being leached. The extent of dissolution of the gangue minerals was manipulated to give the desired chemical consumption of sodium carbonate in the leach. A set of sensitivity studies was carried out, in which the amount of fresh water added to the countercurrent decantation train was varied from a wash ratio of unity to almost zero, the solids content of the thickener underflow in the countercurrent decantation train was set to 40, 45 and 50 percent and the consumption of sodium

¹ The sodium hydroxide and sodium carbonate added were assumed to be solids. In reality there would be more entry points for fresh water, such as incoming sodium hydroxide and sodium carbonate solutions, and in flocculent and gland seal water. For simplicity, these were left off the model for this exercise.

carbonate in the leach section was 10, 20 or 30 kg per ton of solids leached. As the amount of fresh water added to countercurrent decantation and the percentage solids in the underflows changed, so did the quantity of excess barren solution from ion exchange that was required to leave the circuit. The model was set up, somewhat arbitrarily, to maintain a carbonate concentration equivalent to 20 g/L of Na_2CO_3 in the solution leaving the leach. As the dissolution of the gangue minerals varied, the model adjusted the addition of sodium carbonate to the lixiviant. The model also manipulated the addition of sodium hydroxide to the barren solution returning from the ion exchange section to the leach, to convert the bicarbonate in that solution to carbonate.

Figure 2 is a plot of the consumption of sodium carbonate versus the amount of wash water added to the last thickener in the countercurrent decantation train for sodium carbonate consumptions of 10, 20 and 30 kg per ton of dry solids leached, 45 percent solids in the thickener underflows and no returning dam water from the tailings facility. Figure 3 shows the same thing, except that it plots sodium hydroxide. In these graphs the water wash ratio is the amount of fresh water entering the last thickener, divided by the amount of solution in the underflow leaving the last thickener. With these graphs, the amount of barren solution from ion exchange added to thickeners four and six combined is such that an overall wash ratio of unity is maintained for the barren solution as well. As the amount of fresh water added to the final thickener was reduced, the amount of barren solution also going to the final thickener was increased to keep a total wash ratio of unity at the last thickener. As more barren solution went to the last thickener, the total wash ratio at the first to the fourth thickeners decreased.

Figure 2 – Effect of leach chemistry on the consumption of sodium carbonate



As the amount of fresh water added to the countercurrent decantation train reduces, so does the amount of excess barren solution from ion exchange that has to leave the circuit. The curves in Figure 2 show a minimum consumption of sodium carbonate at the point at which the water in the underflow leaving the final thickener balances the fresh water added to the final thickener. As the addition of fresh water is reduced beyond this point, the displacement of carbonate from the slurry continues to decrease, which is why the loss of carbonate rises as fresh water addition is decreased beyond the point at which it is balanced by the water remaining in the consolidated

tailings. When less fresh water is added as wash to the countercurrent decantation train than is retained in the final consolidated tailings, the model adds water to the barren solution from ion exchange returning to the leach section. That water, of course, has no impact on the wash efficiency of the countercurrent decantation train.

Figure 3 – Effect of leach chemistry on the consumption of sodium hydroxide

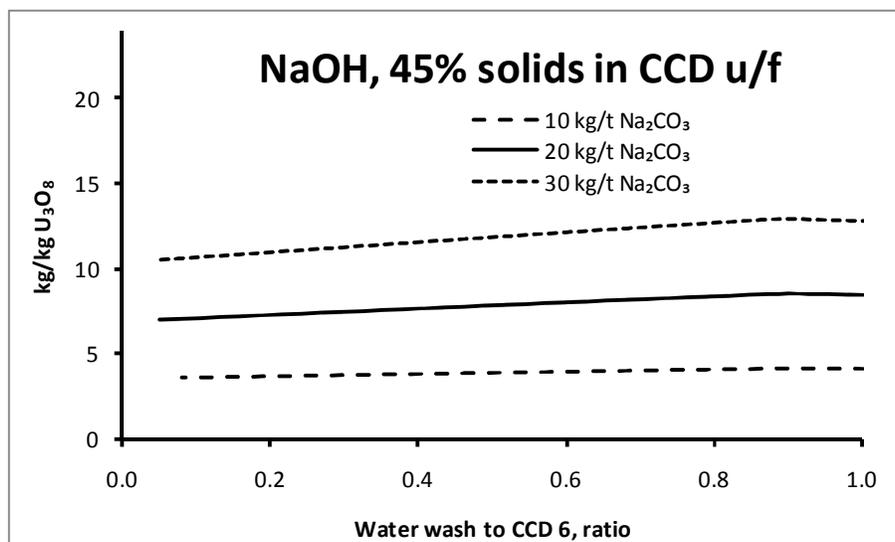


Figure 2 also shows that the consumption of sodium carbonate is affected quite significantly by the leach chemistry. Figure 3 shows that the addition of sodium hydroxide is also affected by the chemistry of the leach. This is readily explained by the chemistry shown in Table 3. As the gangue dissolution increases, more carbonate is consumed and more bicarbonate is generated. The increased consumption of sodium hydroxide is logically required by the increased conversion of bicarbonate to carbonate ahead of leaching. In an actual application the consumption of sodium carbonate and sodium hydroxide would have to be determined experimentally, as would the optimal levels of carbonate and bicarbonate in the solution.

Another factor that would have to be determined experimentally for any actual circuit is the underflow density achievable in thickening. Figure 4 shows the effect of the underflow density in countercurrent decantation on the overall consumption of sodium carbonate. Figure 5 shows the effect of underflow density on the consumption of sodium hydroxide. The consumption of sodium hydroxide is less affected by the underflow density than is the consumption of sodium carbonate. For a chemical consumption of sodium carbonate of 20 kg per ton of solids leached, and a residual concentration of sodium carbonate of 20 g/L, as the underflow density increased from 40 to 50 percent solids, the minimum consumption of sodium carbonate decreased from about 20 to about 17 kg per kilogram of U₃O₈ produced. The importance of maximizing the solids content of the thickener underflows would appear to be obvious. It would also appear to be obvious that the fresh water entering the circuit should do so as wash to the final thickener in the countercurrent decantation train. Using only barren solution from ion exchange would result in substantially higher losses of carbonate to the underflow leaving the countercurrent decantation train and more than double the overall consumption of sodium carbonate.

Figure 4 – Effect of underflow density on the consumption of sodium carbonate

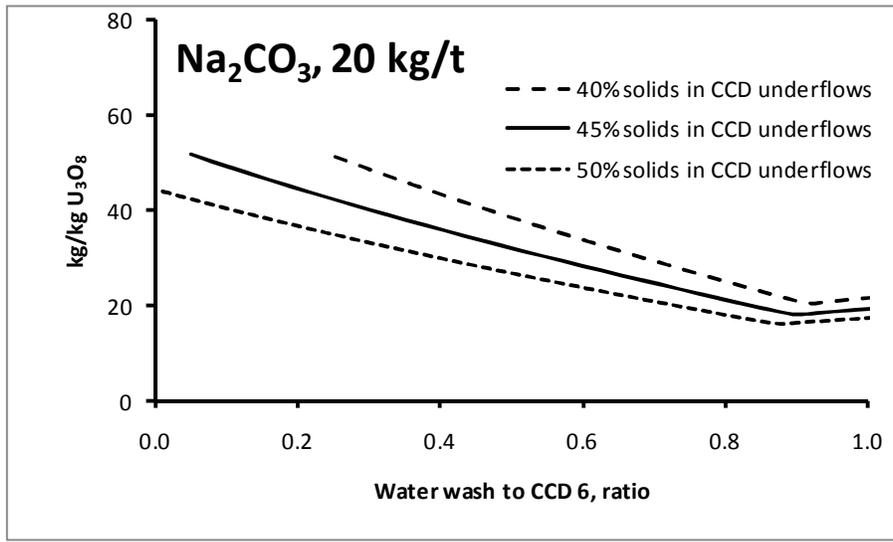
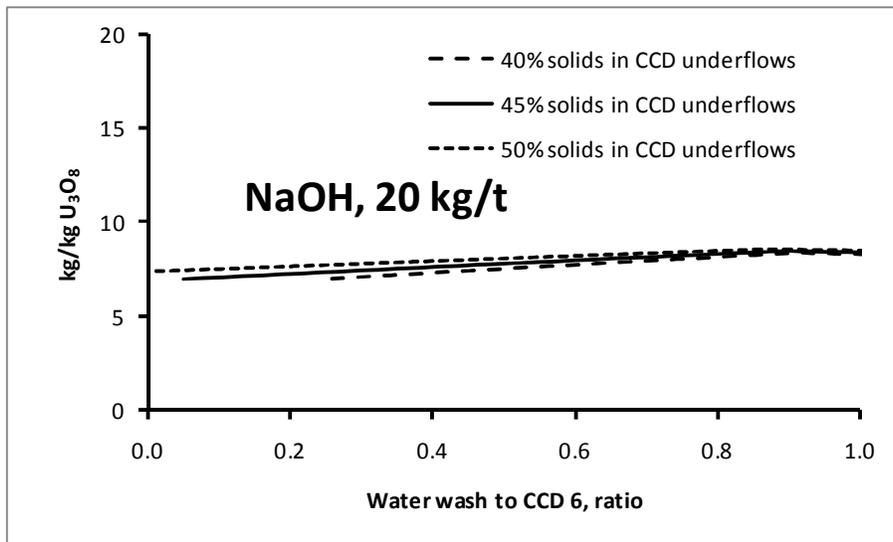


Figure 5 - Effect of underflow density on the consumption of sodium hydroxide



The calculations that generated Figure 2, Figure 3, Figure 4 and Figure 5 were done assuming that no solution returns from the tailings facility. That would imply that either all of the free water is evaporated there, or that not enough consolidation of the final tailings occurs to liberate any solution, which is an over-simplification. Figure 6 shows curves for the overall consumption of sodium carbonate at different levels of evaporation of water on the tailings dam, assuming that the tailings consolidate to 60% solids. For these curves the chemical consumption of sodium carbonate was taken as 20 kg per ton of solids leached and the underflows in the countercurrent decantation train were assumed to contain 45% solids.

The point of minimum consumption of sodium carbonate shifts as the amount of water returning from the tailings facility increases. The reason for that is that the returning solution from the tailings facility displaces some of the fresh water that could otherwise be added as wash to the counter-current decantation train. Figure 7 plots the overall consumption of sodium carbonate in

the circuit and the amount of excess barren solution from the ion exchange section against the wash water ratio at the final thickener in the decantation train, for 5 and 25 percent evaporation of the water at the tailings facility from the consolidating residue. For each extent of evaporation, the minimum in the addition of sodium carbonate occurs at the point on the horizontal axis at which the amount of excess barren solution from ion exchange becomes zero.

Figure 6 – Effect of evaporation on the tailings dam

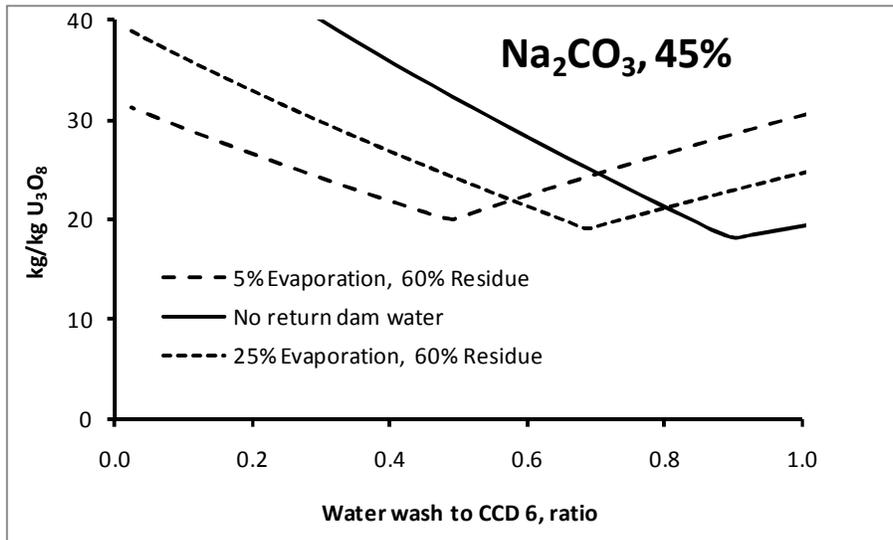


Figure 7 – Effect of evaporation on the excess IX barrens

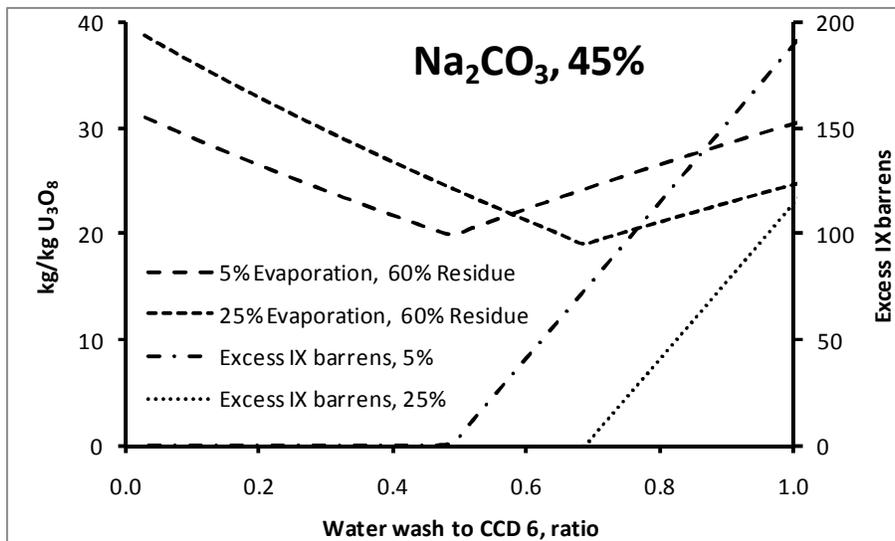


Figure 8 presents the same information slightly differently, showing that as the excess barren solution from ion exchange increases, so does the overall consumption of sodium carbonate.

Figure 9 plots the overall consumption of sodium hydroxide against the amount of excess barren solution from the ion exchange section. The consumption of sodium hydroxide does not appear to be as strongly affected by the overall water balance as the consumption of sodium carbonate.

Figure 8 – Addition of Na_2CO_3 versus IX barrens

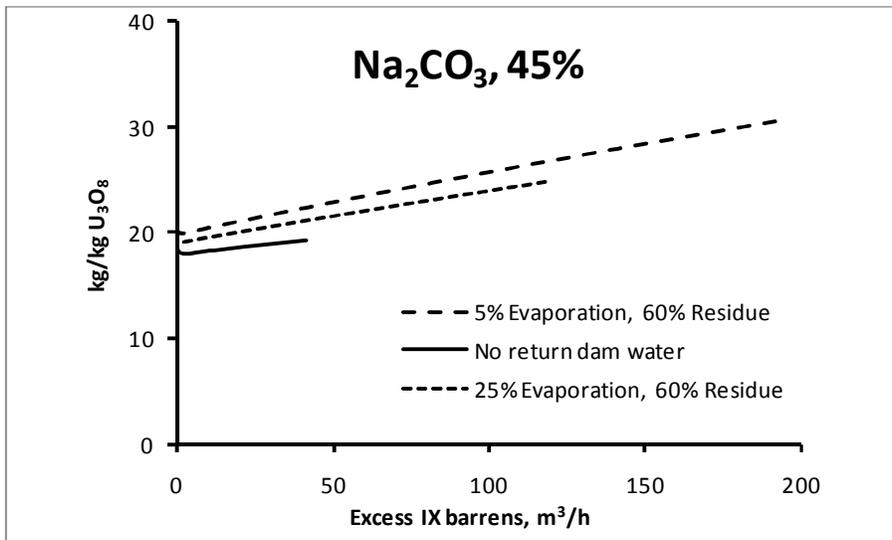
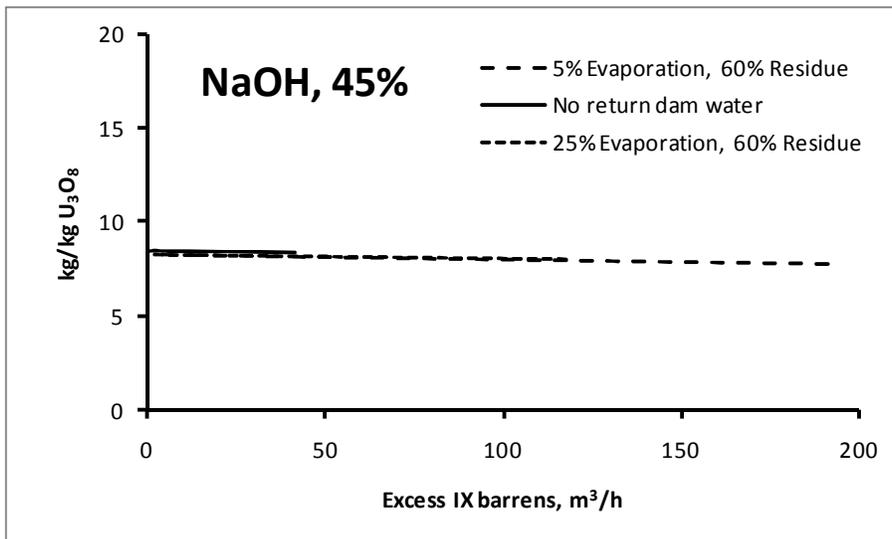


Figure 9 – Addition of NaOH versus excess IX barrens



6. CONCLUSION

The work discussed in this paper was done to study an alkaline circuit for uranium extraction and to examine the overall chloride and water balances. What the study uncovered is that the overall consumption of sodium carbonate and sodium hydroxide is minimized when the amount of fresh wash water used in the separation section is such that there is no excess of barren solution from the ion exchange section that needs to leave the circuit as a bleed and all the incoming fresh water enters as wash to the solid-liquid separation section.

The study presented here is intentionally simplistic. The carbonate and water balances are dominated by the leach and the solid liquid separation sections of the circuit. Experimental work on the leaching and solid liquid separation and washing sections will ultimately be vital for a successful process design.

7. REFERENCES

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