Using Computing Power in Process Development

Mike Dry

Arithmetek Inc. (www.arithmetek.com)

Abstract

This paper presents two techniques for analyzing hydrometallurgical circuits and illustrates them using two worked examples. One is the leaching of laterite using sulfuric acid and the other is the leaching of uranium using sodium carbonate. A spreadsheet-based calculation technique using the stoichiometry of the process is compared to the use of specialized process modeling software.

Contents

Introduction	2
Example 1 - Laterite	3
Calculations	3
Process model	8
Heap leach	8
Iron precipitation	9
Base metal recovery	10
Magnesium precipitation	11
Comparison	11
Example 2 – Uranium	16
Process chemistry	17
Process model	20
Calculations	22
Comparison	30
Conclusion	



Introduction

There are two primary sources from which humanity derives material wealth. One is things that grow and are harvested, which gives us agriculture, fishing, forestry *etc*. The other is materials in the ground that we discover and exploit by mining, beneficiation, metallurgical processing and manufacturing. Civilization as we know it depends heavily on the use of metals that exist in the ground as ores. Geologists discover ores, miners extract them from the earth and metallurgists process them to extract the metals.

No two deposits being identical, the extraction of metal from any given ore requires specifically tailored process equipment. That necessitates appropriate process information on which the design of such equipment can be based, which is where organizations like Mintek make their invaluable contribution to society at large. The process information required for any given situation often has to be generated experimentally, which requires laboratory work and can also entail extended and extensive piloting. Modern desktop and laptop computers now enable the evaluation of envisaged circuits at a much earlier stage than was previously feasible, identifying uncompetitive circuits earlier and substantially enhancing the efficiency of the experimental work that will always be required for the development of a new mine or processing facility.

This paper presents and discusses two examples illustrating the use of computing power to enhance the efficiency of process development. One is the processing of laterite and the other is the extraction of uranium from an ore. Both of these examples are generic and do not use information that was generated under conditions of confidentiality. As such they are simplified, but the principles illustrated have been applied to actual projects. The exact numbers used in these examples are less important than the principles illustrated.

Each of the examples presented is examined in two ways - an approach based on an Excel spreadsheet and calculations around the process chemistry, and a more detailed approach using process modeling software.



Example 1 - Laterite

This example is based on general process knowledge and published information, including the results of leaching tests that happen to have been done by Mintek¹. The key finding of the experimental work was that this particular laterite responds well to leaching at reasonably low additions of sulfuric acid, leading to the speculation that low-cost heap leaching could be appropriate in this instance.

The first eight lines of Table 1 are the published information. The nickel production rate was chosen to give a mine life of close to twenty years.

Ni grade, mass %	1.1
Co grade, mass %	0.034
Cu grade, mass %	0.007
Fe grade, mass %	8.5
Mg grade, mass %	3.5
Extraction by leaching, %	92
H ₂ SO ₄ demand, kg/t	210
Total ore reserve, Mt	31
Assumed Ni production, tpa	15000
Calculated life of mine, years	21

Table 1 – Input information

Calculations

This example assumes the following main sections in the circuit:

- Heap leaching with sulphuric acid.
- Precipitation of iron from the pregnant liquor.
- Precipitation of a bulk hydroxide containing the base metals.
- Precipitation of magnesium from the remaining solution.

¹ http://www.africaneagle.co.uk/african-eagle-projects-dutwa.html



Figure 1 is a block diagram illustrating the basic circuit. The water balance is not addressed in this example, but it could be (and is, in the next example). This exercise is to calculate reagent consumptions and an approximate cost structure, in order to examine the potential viability of the circuit.





The first step is to generate an assemblage of minerals that correctly reproduces the available information on the feed. Typically, the nickel in laterites is present



Page 4 of 34

as nickel oxide incorporated in a goethite-type mineral and in magnesium silicate. The iron is usually present as goethite (FeOOH) and hematite (Fe₂O₃), the relative proportions depending on the degree of weathering of that particular ore. A useful assumption is that acid leaching at low temperature decomposes the goethite but not the hematite, so the proportions of goethite and hematite play an important role in determining the overall consumption of acid. The magnesium silicate is also attacked, leaving silica.

A simple representation of laterite ores is as a mixture of oxides of the valuable metals, goethite, hematite, magnesium oxide and silica. In this example leaching the ore with sulfuric acid consumes 210 kilograms of H_2SO_4 per ton of dry ore. Table 2 shows the acid leach chemistry in simplified form.

$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O$	
$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O$	
$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$	
$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$	
$2\text{FeOOH} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$	

Table 2 – Leach chemistry

The assumption that goethite is dissolved and hematite is not enables the calculation of the amount of goethite that needs to be dissolved to give the observed overall consumption of sulfuric acid. This is a simple acid balance, *viz*.

- In molar units, 1000 kg of dry ore contains:
 - 0.187 kmol of NiO
 - 0.006 kmol of CoO
 - 0.001 kmol of CuO
 - 1.440 kmol of MgO
 - \circ 1.522 kmol of iron, split between FeOOH and Fe₂O₃
- The total consumption of H_2SO_4 is 2.141 kmol per 1000 kg of ore.



The dissolution of NiO, CoO, CuO and MgO accounts for 1.634 kmol of the acid, leaving the balance for the dissolution of FeOOH, forcing the amount of FeOOH dissolved to be 0.338 kmol per 1000 kg of dry ore. Assuming the percentage dissolution of FeOOH to be the same as those of nickel, cobalt and copper (92%) and that the dissolution of MgO is also 92% gives the mineral assemblage listed in Table 3. Hematite accounts for the difference between the total iron and the goethite. Silica is simply the difference between 100% and the sum of the other components. More detailed leach data could just as easily have been used, had that been available.

NiO	1.40
CoO	0.04
CuO	0.01
MgO	5.80
FeOOH	4.10
Fe ₂ O ₃	8.46
SiO ₂	80.18

Table 3 – Laterite representation, mass %

The pregnant liquor from the leach is treated with limestone $(CaCO_3)$ to neutralize residual acid and to precipitate the dissolved iron. This leaves an iron-free solution from which the valuable base metals can be recovered. Table 4 shows the overall chemistry associated with the iron precipitation step. The amount of limestone consumed is fixed by the amount of iron dissolved in the leach and the level of free acid in the solution after leaching.

Table 4 – Iron precipitation

 $\begin{array}{l} \mathsf{H_2SO_4} + \mathsf{CaCO_3} \rightarrow \mathsf{CaSO_4} + \mathsf{H_2O} + \mathsf{CO_2} \\ \\ \mathsf{Fe_2(SO_4)_3} + 3\mathsf{CaCO_3} + \mathsf{H_2O} \rightarrow 3\mathsf{CaSO_4} + 2\mathsf{FeOOH} + 3\mathsf{CO_2} \end{array}$



Page 6 of 34

In this example the nickel, cobalt and copper are precipitated from the iron-free pregnant liquor as a bulk hydroxide, using magnesium oxide. Table 5 shows the overall chemistry assumed for this step. In reality the chemistry is more complex, but this example is deliberately simplified. The precipitate would be washed, dried and sold. Its nickel content would probably be about 50 percent. The consumption of magnesium oxide is fixed by the amounts of nickel, cobalt and copper precipitated and the amount of residual MgO in the precipitate.

Table 5 –	Base	metal	precipitation
-----------	------	-------	---------------

```
\begin{split} \text{NiSO}_4 + \text{MgO} + \text{H}_2\text{O} &\rightarrow \text{Ni}(\text{OH})_2 + \text{MgSO}_4\\ \text{CoSO}_4 + \text{MgO} + \text{H}_2\text{O} &\rightarrow \text{Co}(\text{OH})_2 + \text{MgSO}_4\\ \text{CuSO}_4 + \text{MgO} + \text{H}_2\text{O} &\rightarrow \text{Cu}(\text{OH})_2 + \text{MgSO}_4 \end{split}
```

Calculating the residual magnesium oxide in the mixed hydroxide precipitate (MHP) is straightforward, as follows.

Assumed Ni in MHP: 50 mass % MHP produced: 0.202 kg/ton ore Ni(OH)₂ in MHP: 0.160 kg/ton ore Co(OH)₂ in MHP: 0.005 kg/ton ore Cu(OH)₂ in MHP: 0.001 kg/ton ore Therefore, MgO in MHP: 0.037 kg/ton ore

From this calculation, the residual MgO in the in the MHP is small compared to the amount required to precipitate the base metals.

The barren solution remaining after the precipitation of the base metals contains magnesium that is precipitated with lime, according to the chemistry shown in Table 6. This is necessary to avoid a buildup of magnesium sulphate in the circuit as the process water is recycled.

In reality the CaSO₄ would probably be gypsum (CaSO₄•2H₂O), but that was ignored in this exercise because the overall water balance was not examined.



The amount of lime required can be calculated from the amount of magnesium, which can be calculated from the amount of magnesium leached and the amounts of nickel, cobalt and copper precipitated. Table 7 summarizes the calculated amounts of limestone, magnesia and lime consumed.



 $MgSO_4 + CaO + H_2O \rightarrow Mg(OH)_2 + CaSO_4$



Limestone, as 100% CaCO ₃	63.8
Magnesia, as 100% MgO	7.2
Lime, as 100% CaO	10.0

Process model

The next level of process analysis entails developing a detailed material balance around the circuit in question. (Sometimes a mass/ energy balance is required, but for this example a material balance suffices.) Figure 2 is a diagram of the circuit in more detail, illustrating the circuit as modeled using commercially available software known as AspenPlus[®]. The process model coveres nickel, copper, cobalt, iron, calcium, magnesium and water. The main unit operations are as follows.

Heap leach

Incoming ore is agglomerated with a dilute solution of sulfuric acid and stacked into new heaps. Solution from the old heaps is supplemented with some fresh sulfuric acid and passed through the new heaps. Once a new heap is partially spent it becomes an old heap through which more solution is circulated, supplemented as necessary with fresh sulfuric acid. Once an old heap is



depleted it becomes a spent heap. Water is circulated through the spent heaps to extract the residual acid and dissolved metals and then sent to the old heaps.

Pregnant solution leaving the new heaps proceeds to the iron precipitation section. The process chemistry is as before (Table 2).



Figure 2 – Circuit modeled

Iron precipitation

Limestone is added to the pregnant solution from the heaps to raise its pH and precipitate the ferric iron. The process chemistry is as before (Table 4). The



Page 9 of 34

temperature is raised to 60°C by the injection of live steam to ensure that the iron is precipitated as goethite rather than ferric hydroxide². The resulting slurry of goethite and gypsum is thickened and the underflow is washed with recycled water in a counter-current decantation train. The washed residue leaves the circuit and the supernatant from the counter-current decantation train joins the supernatant from the preceding thickener. The combined solution proceeds to the base metal recovery section.

Base metal recovery

The solution from the iron removal section is contacted with magnesium oxide to raise the pH sufficiently to precipitate the base metals. Live steam is injected to raise the temperature to 65 °C. The chemistry is slightly more complex than before, to introduce a difference between idealized and more realistic conditions. Some sulfate is included in the precipitate and dissolved carbonate from the limestone used in the iron removal step combines with some of the magnesium oxide to form magnesium carbonate, reducing the overall efficiency of utilization of the magnesium oxide. The associated chemistry is illustrated in Table 8. In this process model, the precipitate was assumed to contain 5% sulfate.

Table 8 – Base metal precipitation

$$\begin{split} \mathsf{NiSO}_4 + \mathsf{MgO} + \mathsf{H}_2\mathsf{O} &\Rightarrow \mathsf{Ni}(\mathsf{OH})_2 + \mathsf{MgSO}_4\\ \mathsf{CoSO}_4 + \mathsf{MgO} + \mathsf{H}_2\mathsf{O} &\Rightarrow \mathsf{Co}(\mathsf{OH})_2 + \mathsf{MgSO}_4\\ \mathsf{CuSO}_4 + \mathsf{MgO} + \mathsf{H}_2\mathsf{O} &\Rightarrow \mathsf{Cu}(\mathsf{OH})_2 + \mathsf{MgSO}_4\\ \mathsf{4NiSO}_4 + \mathsf{3MgO} + \mathsf{3H}_2\mathsf{O} &\Rightarrow \mathsf{NiSO}_4 \bullet \mathsf{3Ni}(\mathsf{OH})_2 + \mathsf{3MgSO}_4\\ \mathsf{4CoSO}_4 + \mathsf{3MgO} + \mathsf{3H}_2\mathsf{O} &\Rightarrow \mathsf{CoSO}_4 \bullet \mathsf{3Co}(\mathsf{OH})_2 + \mathsf{3MgSO}_4\\ \mathsf{MgO} + \mathsf{CO}_2 &\Rightarrow \mathsf{MgCO}_3 \end{split}$$

² Goethite has much better solid-liquid separation characteristics than ferric hydroxide.



The precipitated base metals are settled, filtered and washed with water. The washed precipitate leaves the circuit and the combined filtrate proceeds to the magnesium precipitation section.

Magnesium precipitation

Lime is used to raise the pH to about 10 and precipitate magnesium from the solution leaving the base metal recovery section. The process chemistry is as before (Table 6). Live steam is injected to keep the temperature at 65 °C. The resulting slurry is thickened and the thickened slurry leaves the circuit. The thickener overflow is recycled to the countercurrent decantation section as wash.

Comparison

Table 9 shows the comparison between the numbers for reagent consumption calculated *via* the spreadsheet and the numbers from the process model.

Reagent	Calculation	Model
Limestone, as 100% CaCO ₃	63.8	68.5
Magnesia, as 100% MgO	7.2	6.3
Lime, as 100% CaO	84.4	81.9

Table 9 – Reagent consumptions, kg/ton ore

The calculated values and those from the process model are not identical but do seem to be close enough for the spreadsheet approach to be useful. The following simple economic analysis shows the impact of the differences on the potential viability of this circuit. The unit costs and metal prices are listed in Table 10 and Table 11. For this exercise the exact values are less important than the technique illustrated. The numbers are reasonable but not necessarily correct.



Reagent	\$/t
H_2SO_4	100
CaCO ₃	50
NaOH	1000
MgO	300
CaO	200

Table 10 – Unit costs

Table 11 – Metal prices

Metal	\$/lb
Ni	5.00
Co	20.00
Cu	1.50

The bulk hydroxide was assumed to sell at a price equivalent to 85 percent of the contained nickel price and 90 percent of the contained cobalt and copper prices.

Mining, ore preparation and power consumed by pumping and agitation all contribute to the overall operating cost. The numbers in Table 12 come from the spreadsheet-based approach. The numbers that do not come from the reagent costs were extrapolated from a recent design for a nickel production circuit of similar capacity to that assumed here. These numbers are necessarily uncertain and serve more as place holders for better inputs than as plausible values in themselves. Their impact is small compared to the costs calculated for acid, limestone and lime. The power consumption for electrolysis is based on fairly typical values in conventional electrolysis of 3.5 kWh per kg of metal for nickel and cobalt and 2.0 kWh per kilogram of copper.

In Table 12, the headings "kg/t" or "kWh/t" mean kilograms or kilowatt hours per ton of ore leached. The heading "\$/t" is for the unit costs and the heading "\$/lb"



is the variable cost per pound of nickel produced. The currency assumed is US dollars. The calculated operating costs are summarized in Table 13.

Reagents	kg/t	\$/t	\$/lb Ni
H ₂ SO ₄ to Ni/Co/Cu	17.5	100	0.08
H ₂ SO ₄ to Fe	62.5	100	0.28
H ₂ SO ₄ to Mg	129.9	100	0.58
CaCO ₃	63.8	50	0.14
MgO	7.2	300	0.10
CaO	84.3	200	0.76
Power consumption	kWh/t	\$/kWh	\$/lb Ni
Mining and ore prep.	5.0	0.1	0.02
Agitation, pumping	2.0	0.1	0.01
Electrolysis of Ni/Co		0.1	
	· · ·		
М	Mining cost (\$5/t ore)		
Reagent cost			1.84
Energy cost			0.03
Projected variable cost			2.37

Table 12 – Variable costs (Spreadsheet calculation)

Table 13 – Operating costs, \$ million/year

Labour cost (100 people @\$50k/year)	5
Consumables cost (1%/y of capex)	5
Services (assume same as energy)	1
Variable costs	78



Table 14 lists some published capital costs for nickel extraction circuits. Figure 3 shows these numbers (as filled circles) in graphical form, the costs on a logarithmic axis and the production capacity on a linear axis. The line is a best straight line through the data points. The hollow circle is the corresponding capital cost extrapolated from the data points for the nickel production capacity of this exercise. The published capital costs are from projects involving pressure oxidation in autoclaves and are probably be biased high in the context of this exercise. For want of better information, however, these numbers were used.

Company	Туре	kt/y	Capex
Skye (2005)	Scoping	20	508
Ambatovy	Pre-feas.	60	2500
Goro	Bankable	60	3200
Ravensthorpe	Bankable	50	2100

Table 14 – Published capital costs

Figure 3 – Published capital costs



The metal prices in Table 11 were used, along with the calculated capital and operating costs, to generate simple economic models based on the spreadsheet



calculations and on the output of the process model. The results from these economic models are shown in Table 15 and Table 16. The columns for years 8 to 21 are the same as for years 7 and 22.

Year	1	2	3	4	5	6	7	22
Revenue			39.7	79.4	158.9	158.9	158.9	158.9
Costs	206.1	206.1	30.6	39.1	89.2	89.2	89.2	89.2
Margin	-206.1	-206.1	9.1	40.3	69.6	69.6	69.6	69.6
Tax	0.0	0.0	0.0	0.0	0.0	0.0	11.0	13.9
Profit	-206.1	-206.1	9.1	40.3	69.6	69.6	58.6	55.7

Table 15 – Economic model based on the spreadsheet calculations

10.0%
7.9%

Guesstimated capital cost, \$ million	412

Table 16 – Economic model based on the process model

Year	1	2	3	4	5	6	7	22
Revenue			39.7	79.4	158.9	158.9	158.9	158.9
Costs	206.1	206.1	30.6	39.1	89.1	89.1	89.1	89.1
Margin	-206.1	-206.1	9.2	40.4	69.8	69.8	69.8	69.8
Tax	0.0	0.0	0.0	0.0	0.0	0.0	11.2	14.0
Profit	-206.1	-206.1	9.2	40.4	69.8	69.8	58.6	55.8

Before-tax IRR	10.1%
After-tax IRR	7.9%

Guesstimated capital cost, \$ million

412

I terms of the calculated internal rates of return, the differences between the numbers from the spreadsheet calculations and those from the process model are insignificant.

The message behind this illustration is that a reasonable knowledge of the chemistry of any circuit under consideration, coupled with adequate spreadsheet skills, enables one to analyze a circuit quite effectively using minimal input information and without having to acquire and learn to use specialized software.



Example 2 – Uranium

In the first example the reagent is sulfuric acid and is consumed completely, which makes complicated recycle calculations unnecessary in the spreadsheetbased approach. Once the spreadsheet calculations have shown a circuit to be worthy of further effort, process modeling naturally takes care of the recycles. A countercurrent decantation train, for example, requires recycle calculations that are not necessary for the initial calculations if there is no reagent left to recycle. However, there are circuits in which the reagent is not depleted after leaching. In such cases, the recycle of reagent needs to be considered in preliminary calculations to avoid distorting the results excessively.

The second example chosen for this paper is such a case. In the extraction of uranium, the reagent can be acid or alkali. This example examines a circuit entailing carbonate leaching. Figure 4 is a block diagram illustrating the circuit chosen. An ore containing hexavalent uranium was selected. Table 17 shows the input data used for this example. These numbers are similar to published information from the Langer Heinrich Uranium project in Namibia, merely to give some realism to this study³.



Figure 4 – Uranium circuit

³ http://www.paladinenergy.com.au/Portals/0/File/brochures/09.02%20Langer%20Heinrich%20Project%20-%20February%202009.pdf.



U_3O_8 grade, mass %	0.06
Total ore reserve, Mt	51
Assumed leach extraction, %	99
Assumed life of mine, years	20
Calculated U_3O_8 dissolution, tpa	1515

Table 17 - Ore assays, parts per million

Table 18 is a calculated mineral assemblage representing the ore in Table 17. 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.

Table 18 – Representation of the ore, mass %

$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$	0.10
$NaCa_2Fe_4Al_3Si_6O_{22}(OH)_2$	2
KAl ₃ Si ₃ O ₁₀ Cl ₂	3
CaSO ₄	0.5
CaCO₃	10
SiO ₂	84.4

Process chemistry

The mineralogy of the ore largely dictates the chemistry of the leach. Table 19 shows the stoichiometry used to represent the leaching of this ore in a solution containing sodium carbonate. The last equation is the carbonate-bicarbonate equilibrium that buffers the pH of the solution.

For this example the assumed dissolution of uranium is 99.5 percent. The extent of dissolution of the clay minerals was assumed to be such that the chemical consumption of sodium carbonate is 20 kg per ton of solids leached. The calcium



sulfate was assumed to convert completely to calcium carbonate and the quartz (SiO₂) was assumed to be inert.

Table 19 – 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 diuranate⁴ (see Table 22 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.

For this exercise, countercurrent decantation was assumed for the solid liquid separation step between the leach and the ion exchange sections. However the solid-liquid separation is done, it is necessary because the barren solution from ion exchange has to be returned to the leaching section to recycle carbonate.

Strong base resins are used to extract the anionic uranium carbonate complex. Table 20 shows chemistry representing the extraction stage of the ion exchange sequence. The symbol (R_4N) • represents the resin. The design objective for the ion exchange section is to maximize the extraction of uranium, for which reason this example assumes complete extraction of uranium. The extent to which species like vanadium, sulphate and chloride are co-extracted depends on the exact resin chosen and the exact process conditions.

⁴ Mukherjee, C. K. Gupta and T.K. *Hydrometallurgy in Extraction Processes, Volume 1.* s.l. : CRC Press



$2(R_4N)_2 \cdot CO_3 + UO_2(CO_3)_3^{4-} \rightarrow (R_4N)_4 \cdot UO_2(CO_3)_3 + 2CO_3^{2-}$
$(R_4N)_2 \bullet CO_3 + HVO_4^{2\text{-}} \rightarrow (R_4N)_2 \bullet HVO_4 + CO_3^{2\text{-}}$
$(R_4N)_2 \cdot CO_3 + SO_4^{2-} \rightarrow (R_4N)_4 \cdot SO_4 + CO_3^{2-}$
$(R_4N)_2 \bullet CO_3 + 2CI^- \rightarrow 2(R_4N) \bullet CI + CO_3^{2-}$

Table 20 – Ion-exchange: extraction

Uranyl carbonate can be eluted from strong base resin by solutions containing one molar carbonate, bicarbonate, sulphate or chloride⁵. Table 21 shows the relevant chemistry. The reactions for the elution of vanadium, sulphate and chloride with carbonate are the reverse of the loading reactions and the reactions for elution with sulphate, bicarbonate or chloride are analogous to the elution reactions using carbonate.

Table 21 – Ion exchange: elution

$$\begin{aligned} (\mathsf{R}_4\mathsf{N})_4 \bullet \mathsf{UO}_2(\mathsf{CO}_3)_3 + 2\mathsf{Na}_2\mathsf{CO}_3 &\to 2(\mathsf{R}_4\mathsf{N})_2 \bullet \mathsf{CO}_3 + 4\mathsf{Na}^+ + \mathsf{UO}_2(\mathsf{CO}_3)_3^4 \\ (\mathsf{R}_4\mathsf{N})_4 \bullet \mathsf{UO}_2(\mathsf{CO}_3)_3 + 4\mathsf{Na}\mathsf{CI} &\to 4\mathsf{R}_4\mathsf{N}\bullet\mathsf{CI} + 4\mathsf{Na}^+ + \mathsf{UO}_2(\mathsf{CO}_3)_3^4 \\ (\mathsf{R}_4\mathsf{N})_4 \bullet \mathsf{UO}_2(\mathsf{CO}_3)_3 + 2\mathsf{Na}_2\mathsf{SO}_4 &\to 2(\mathsf{R}_4\mathsf{N})_2 \bullet \mathsf{SO}_4 + 4\mathsf{Na}^+ + \mathsf{UO}_2(\mathsf{CO}_3)_3^4 \end{aligned}$$

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.

Typically, the eluate from ion exchange would contain uranium at some desired level of grams per liter. Adding sodium hydroxide to the eluate raises its pH and causes sodium diuranate (SDU) to precipitate. Table 22 shows the associated chemistry, assuming uranyl carbonate as the starting point.

⁵ Fleming, C.A. *The chemistry of uranium recovery from leach solutions.* Johannesburg, South Africa : Vacation School: Uranium Ore Processing, National Institute for Metallurgy, 27-31 July 1981



Table 22 - Precipitation and recovery of uranium

$$2UO_{2}(CO_{3})_{3}^{4^{-}} + 6OH^{-} + 2Na^{+} \rightarrow Na_{2}U_{2}O_{7} + 6CO_{3}^{2^{-}} + 3H_{2}O$$

$$Na_{2}U_{2}O_{7} + 3H_{2}SO_{4} \rightarrow 2Na^{+} + 2UO_{2}^{2^{+}} + 3SO_{4}^{2^{-}} + 3H_{2}O$$

$$(4+x)H_{2}O + UO_{2}^{2^{+}} + H_{2}O_{2} \rightarrow UO_{4}\bullet xH_{2}O + 2H_{3}O^{+}$$

As uranium hydroxide is precipitated, some acid is released and is neutralized with sodium hydroxide. The SDU is then re-dissolved in sulfuric acid and water and hydrogen peroxide is added to convert the dissolved uranium to precipitated uranium peroxide.

Process model

Figure 5 is a diagram illustrating the process model used in the second example.

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 19 occur.

The leached slurry proceeds to a six-thickener countercurrent decantation (CCD) 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 to minimize the loss of carbonate to the final thickener underflow.

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 by evaporation. The balance is recovered as return dam water that joins the barren solution from the ion exchange section returning to the leach.





Figure 5 – Uranium process model

In reality, the overflow from the first thickener in the CCD 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.

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 is adjusted to give 10 g/L of U_3O_8 in the eluate.



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 the ion exchange section would return to the leach in the barren solution. Either way, these species are recycled to the leach, possibly minus any part rejected with the sodium sulfate effluent.

The pH of the eluate from the ion exchange section is raised with sodium hydroxide, causing sodium diuranate to precipitate. In this exercise, 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, after which 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 consumed by 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.

Calculations

The calculations around the uranium extraction circuit require some basic assumptions. Table 23 lists the assumptions used. The first two assumptions enable the calculation of the mass per hour of dry solids and liquids in the incoming ore. (If the actual moisture content of the ore is known, so much the better.) The hourly rate of dry solids entering in the ore is calculated from the required annual dissolution of U_3O_8 from Table 17, divided by the U_3O_8 content of the ore and the percentage dissolution of uranium. The water in the incoming ore is calculated from its moisture content. The total amount of liquid entering



the leach is calculated from the amount of solids entering the leach and the solidto-liquid ratio assumed for the leach.

Operating days per year	350
Moisture in incoming ore, mass %	5
S/L ratio to leach, kg/m ³	300
Na_2CO_3 consumption in leach, kg/t	20
Residual Na ₂ CO ₃ ex leach, g/L	20
S/L ratio ex CCD, kg/m ³	815
S/L ratio of final tailings, kg/m ³	1236
Evaporation on tailings dam, %	5
Water wash ratio to CCD 6	0.32
IX barrens wash ratio to CCD 4	1.00
Uranium recovery in IX, etc., %	100
Na ₂ CO ₃ in IX eluant, mol/L	1.0
U ₃ O ₈ in IX eluate, g/L	10
NaOH ex SDU precipitation, g/L	10.0
Times stoichiometric H ₂ SO ₄ to SDU	1.1
Times stoichiometric H_2O_2 to UO_4	1.5

The percentage dissolution of the gangue minerals is calculated from the stoichiometry shown in Table 19 and the assumed consumption of carbonate in the leach. The fractional conversion for the first reaction is set by the assumed dissolution of uranium. The first reaction releases OH⁻ ions that react with bicarbonate formed by the other reactions, thereby regenerating some of the carbonate. The second and third reactions consume eight and seven molar units, respectively, of carbonate per molar unit of the mineral concerned dissolved. The reaction between calcium sulfate and calcium carbonate consumes one molar unit of carbonate per molar unit of calcium sulfate dissolved. Once the gangue dissolution has been calculated, stoichiometry enables the calculation of the amount of solids remaining after the leach and of



Page 23 of 34

the amount of water generated in the leach. The amount of liquid entering the leach and the amount of water generated in the leach give the amount of liquid leaving the leach. Those numbers lead to the concentration of uranium in the solution leaving the leach. The concentrations of vanadium, sulphate and chloride in the solution leaving the leach are affected by the recycle of these species in the solutions returning to the leach. Since their only exit is in the final consolidated tailings, their concentrations can be calculated as the amounts dissolved in the leach divided by the volume of solution in the final consolidated tailings, which is calculated from the solids leaving the leach and the assumed solid-liquid ratio of the consolidated tailings. The amount of sodium carbonate in the solution leaving the leach is fixed as an assumption. Table 24 shows the results of these calculations, along with the corresponding numbers from the process model.

ltem	Calculation	Model
Solids to leach, t/h	304	304
Water in incoming ore, m ³ /h	16	16
Total solution to leach, m ³ /h	1012	1012
Gangue dissolution in leach, %	23	28
Solids ex leach, t/h	299	302
Solution ex leach, m ³ /h	1012	1020
U_3O_8 in solution ex leach, g/L	0.18	0.18
V in solution ex leach, g/L	0.14	0.26
SO_4^{2-} in solution ex leach, g/L	4.38	8.33
Cl ⁻ in solution ex leach, g/L	1.42	3.26
Na_2CO_3 in solution ex leach, g/L	20	20
$NaHCO_3$ in solution ex leach, g/L	3	3

Table 24 – L	each ca	lculations
--------------	---------	------------

The amount of barren solution from the ion exchange section returning to the leach section is simply the total amount of liquid entering the leach, minus the amounts in incoming ore, return dam solution and the alkaline solution returning



from the precipitation of sodium diuranate. The composition of the barren solution comes from calculations around the CCD train, discussed next.

The solid-liquid ratio of the washed underflow leaving the CCD section is fixed by assumption. Since the amount of solids leaving the leach is the same as that leaving the CCD section, the amount of liquid in the underflow leaving the CCD section can be calculated from the assumed solid-liquid ratio of the underflow. The amount of solution permanently locked in the final consolidated tailings can be calculated similarly, from the solids leaving the leach and the assumed solid-liquid ratio of the consolidated tailings. The difference between the liquid in the CCD underflow and the liquid locked in the consolidated tailings, less the assumed percentage lost by evaporation, is the volume of the return dam water. The amounts of barren solution from the ion exchange section and incoming wash water added to the CCD train can be calculated from the respective assumed wash ratios. The wash ratio is defined as the amount of wash solution entering divided by the amount of solution in the final underflow leaving the CCD section. For this exercise a wash ratio of unity was assumed for the barren solution from the ion exchange section.

The CCD train contains six thickeners in this example. The amounts of solid and liquid entering from the leach section have been calculated and the amounts of wash solution (barren liquor from the ion exchange section and incoming water) can be calculated from the relevant wash ratios. Assuming conservation of volume across the CCD train and that all the solids report to the thickener underflows enables one to set up liquid volume balances across each thickener and thereby calculate the flows around each thickener, starting at the final thickener and moving back through the train. The concentration profiles of uranium, vanadium, sulfate, chloride, carbonate and bicarbonate down the CCD train can easily be found using Solver (in an Excel spreadsheet) to search for values that close the respective balances across each thickener. Table 25 shows the results of these calculations.



Store	m	³ /h			Concentr	ation, g/L		
Slaye	Liquid	Slurry	U ₃ O ₈	V	SO4 ²⁻	Cl	Na ₂ CO ₃	NaHCO ₃
Feed		1012	0.18	0.14	4.38	1.42	20.0	3.1
CCD1	1128	367	0.15	0.13	4.29	1.68	19.6	3.0
CCD2	483	367	0.11	0.13	4.10	1.61	18.7	2.9
CCD3	483	367	0.07	0.12	3.95	1.55	18.0	2.8
CCD4	483	367	0.04	0.12	3.84	1.51	17.5	2.7
IX barrens	116		0.00	0.14	4.38	1.42	20.0	3.1
CCD5	367	367	0.03	0.11	3.56	1.40	16.2	2.5
CCD6	367	367	0.01	0.10	3.27	1.29	15.0	2.3
Water	116		0.00	0.00	0.00	0.00	0.0	0.0
IX barrens	251		0.00	0.14	4.38	1.42	20.00	3.10

Table 25 – CCD calculations (Spreadsheet)

Store	Balance, Out/In								
Slage	$U_{3}O_{8}$ V SO_{4}^{2-}		Cl	Na ₂ CO ₃	NaHCO ₃				
CCD1	100%	100%	100%	100%	100%	100%			
CCD2	100%	100%	100%	100%	100%	100%			
CCD3	100%	100%	100%	100%	100%	100%			
CCD4	100%	100%	100%	100%	100%	100%			
CCD5	100%	100%	100%	100%	100%	100%			
CCD6	100%	100%	100%	100%	100%	100%			

The numbers in the columns headed "Liquid" and "Slurry" are the liquid volumetric flows in the overflows and underflows, respectively, from the different thickeners. The solution leaving stage 6 of the CCD train is the solution going to the tailings dam. The composition of the return dam water is calculated from that of the solution leaving the CCD train by using the assumed percentage of volume loss due to evaporation on the tailings dam. The number in the column headed Liquid and the row labeled CCD 1 is the volumetric flow of supernatant going from the CCD train to the ion exchange section. For these calculations, the volume of barren solution leaving the ion exchange section was assumed to be the same as the volume of pregnant solution entering ion exchange.

Because water enters the circuit with the incoming ore and as wash water in the filtration of the precipitated sodium diuranate and the final uranium product, a water wash ratio of unity in the CCD train would introduce more water to the circuit than can be recycled. Therefore, the water wash ratio has to be less than



Page 26 of 34

unity and some carbonate lost to the final tailings. (In fact, not losing some carbonate to the final tailings would eliminate the bleed of vanadium, sulphate and chloride from this circuit, leading to an excessive buildup of these impurities.) The volume of wash water to the CCD train has to be adjusted such that the overall volume balance is satisfied. If too much wash water is added, there will be some excess barren solution from the ion exchange section. The volume of excess barren solution is calculated from the total volume leaving the ion exchange section, which is the same as that of the pregnant solution leaving the CCD train, minus the volumes of barren liquor returned directly to the leach and used as wash in the CCD train, minus the volume of wash water added to the CCD train. The volume of wash water added to the CCD train. The volume of wash water added to the CCD train.

The calculated recoveries of uranium and carbonate across the CCD train are listed in **Error! Reference source not found.**, along with the corresponding results from the process model.

Item	Calculation	Model
U ₃ O ₈ recovery over CCD, %	97.1	98.4
U_3O_8 lost to residue, %	1.9	1.1
Carbonate recovery over CCD, %	80.1	86.5
Carbonate lost to residue, %	13.1	8.9

Table 26 - Results of CCD calculations

The uranium recovery is higher than the carbonate recovery because the barren solution from ion exchange is depleted in uranium and is therefore able to displace uranium from the slurry but not depleted in carbonate and thus not able to displace carbonate from the slurry. The water wash ratio required for zero excess barren solution from ion exchange turns out to be about 0.29, hence the lower recovery of carbonate.



Resin selectivity ratios can be used to calculate the distribution of species like vanadium, sulfate and chloride across the ion exchange section. The values would depend on the specific resin chosen. For this example, the following values were guessed:

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

The selectivity ratio is defined as the ratio of the concentration of uranium on the resin to the concentration of uranium in solution, divided by the ratio of the concentration of the other species on the resin to the concentration of that species in solution. The units used cancel, making the selectivity dimensionless.

Assuming complete elution of the resin allows a computational "short cut". The selectivity ratio for uranium over another species is given by:

Selectivity =
$$\frac{[U]_{R}/[U]_{S}}{[X]_{R}/[X]_{S}}$$

Where U refers to uranium, X refers to the other species, the subscripts R and S denote the resin or the solution phase, respectively, and the square brackets denote concentration. Multiplying the resin concentrations by the movement of resin and the solution concentrations by the solution flow cancels out between the top and bottom and gives the selectivity ratio in terms of the flows of uranium and the other species:

Selectivity = $\frac{(U \text{ flow})_R/(U \text{ flow})_S}{(X \text{ flow})_R/(X \text{ flow})_S}$

Assuming complete elution, the flows of uranium and the other species on the resin, as it moves from loading to elution, are the same as the flows of uranium and the other species in the eluate. Re-arranging the above equation gives:

$$\frac{(X \text{ flow})_{R}}{(X \text{ flow})_{S}} = \frac{(U \text{ flow})_{R}/(U \text{ flow})_{S}}{\text{Selectivity}}$$



In terms of the extractions of uranium and species X across the ion exchange section, therefore:

Extraction of X = $\frac{\text{Extraction of U}}{\text{Selectivity}}$

Assuming no volume change between eluant and eluate enables the calculation of the concentration of species X in the eluate from its calculated extraction.

Fixing the concentration of uranium in the ion exchange eluate fixes the volume of eluant required. Assuming no volume change from eluant to eluate makes that a simple calculation. Table 27 gives the results of the calculations around the ion exchange section, alongside the corresponding numbers from the process model.

Item	Calculation	Model
Pregnant liquor to IX, m ³ /h	1119	1236
U_3O_8 in PLS to IX, g/L	0.15	0.14
V in PLS to IX, g/L	0.13	0.2
SO_4^{2-} in PLS to IX, g/L	4.30	7.9
Cl⁻ in PLS to IX, g/L	1.40	3.1
Na ₂ CO ₃ in PLS to IX, g/L	19.6	18.4
$NaHCO_3$ in PLS to IX, g/L	3.0	2.7
IX eluant/eluate, m ³ /h	17	18
U_3O_8 in IX eluate, g/L	10	10
V in IX eluate, g/L	0.1	0.4
SO4 ²⁻ in IX eluate, g/L	1.4	2.7
Cl⁻ in IX eluate, g/L	0.2	0.4
CO ₃ ²⁻ in IX eluate, g/L	52	52

Table 27 – Calculations around ion exchange

Assuming no volume change from the addition of sodium hydroxide to the eluate to precipitated sodium diuranate keeps the volume of solution leaving that step and returning to the leach the same as the volume of the eluate. (This does



Page 29 of 34

ignore the volume of wash water used for the filtration of the sodium diuranate, but that is small compared to the other flows.)

The amount of sodium hydroxide used to precipitate sodium diuranate can be calculated from the relevant chemistry and from the assumed residual level of sodium hydroxide in solution after precipitation. The amount of sulfuric acid needed to re-dissolve the sodium diuranate and the hydrogen peroxide needed to oxidize it are calculated from the relevant stoichiometry and the assumed excess quantities. Table 28 gives the numbers calculated around the uranium recovery section alongside the corresponding values from the process model.

Item	Calculation	Model
NaOH to SDU precipitation, t/h	0.25	0.25
Na ₂ U ₂ O ₇ ex SDU precipitation, t/h	0.20	0.20
H_2SO_4 to SDU re-dissolution, t/h	0.10	0.10
H_2O_2 to UO_4 precipitation, t/h	0.03	0.03
NaOH to UO4 precipitation, t/h	0.06	0.07
Na_2SO_4 ex UO ₄ precipitation, t/h	0.13	0.15

Table 28 – Calculations around uranium recovery

Comparison

As might be expected, there are some differences between the numbers calculated using the spreadsheet approach and those from the process model. The point of the spreadsheet approach being an initial evaluation on the viability of the circuit concerned, it is of interest to generate and compare simple cash flow analyses based on numbers from the two approaches. Table 29 lists the reagent costs used for this part of the exercise.



Sodium carbonate	300
Sodium hydroxide	500
Sulphuric acid	300
Hydrogen peroxide	3000

Table 29 – Reagent prices, \$/t

Table 30 and Table 31 list the reagent consumptions calculated using the spreadsheet approach and those generated using the process model.

Cost Reagent per ton of ore per kg of U₃O₈ distribution Na₂CO₃ 21 36 74% NaOH 4 6 21% H_2SO_4 0.3 0.6 1% 4% H_2O_2 0.1 0.2

Table 30 – Reagent consumptions (Spreadsheet)

Table 31- Reagent consumptions (Process model)

Reagent	per ton of ore	per kg of U_3O_8	Cost distribution
Na ₂ CO ₃	12	21	58%
NaOH	5	8	36%
H_2SO_4	0.3	0.6	2%
H_2O_2	0.1	0.2	5%

The Langer Heinrich plant in Namibia, a circuit producing 260 million pounds of U_3O_8 per year, cost US\$92 million⁶. Scaling that number to the production used

⁶ http://www.paladinenergy.com.au/Portals/0/File/brochures/09.02%20Langer%20Heinrich%20Project%20-%20February%202009.pdf



in this example, using an exponent of 0.6, gives a capital cost of \$107 million for the hypothetical circuit of this exercise.

An internet search on 24 April 2009 showed a uranium price of about \$40 per pound of U_3O_8 .

These numbers were used to generate the cash flow analyses shown in Table 32 and Table 33. The initial evaluation using the spreadsheet-based calculations gave results not significantly different to those from the process model.

Year	1	2	3	4	5	6	21	22
Capital expenditure	53	53						
Variable costs			22	22	22	22	22	22
Fixed costs			12	12	12	12	12	12
Revenue			33	67	133	133	133	133
Margin	-53	-53	-1	33	99	99	99	99
Tax	0	0	0	0	7	30	30	30
Cash flow	-53	-53	-1	33	92	70	70	70
Internal rate of return :	NP	V at 10)% disc	count ra	ate: \$	\$315 m	illion	

Table 32 – Cash flow analysis (Spreadsheet)

Year	1	2	3	4	5	6	21	22
Capital expenditure	53	53						
Variable costs			16	16	16	16	16	16
Fixed costs			12	12	12	12	12	12
Revenue			33	67	133	133	133	133
Margin	-53	-53	5	39	105	105	105	105
Tax	0	0	0	0	13	32	32	32
Cash flow	-53	-53	5	39	93	74	74	74
Internal rate of return :	NP	V at 10)% disc	count ra	ate: \$	6344 m	illion	

Table 33 – Cash flow analysis (Process model)



This shows that, as in the first example, doing preliminary calculations on a spreadsheet does generate useful numbers. Naturally, reasonable assumptions need to be made and the calculations need to be done with due diligence and appropriate care.

Conclusion

The calculations illustrated in this paper presuppose that the amount of ore in the deposit concerned is sufficient to sustain a viable rate of production over a useful project life. In the case of a new deposit, the calculation of reserves would entail fieldwork and consume substantial amounts of money. Doing calculations such as those presented here, based on very preliminary experimental work, would yield information relevant to business decisions on whether or not to undertake the expense of proving up any particular deposit.

What is very important in both of the examples presented in this paper is what happens in the leach – the extraction of metals from ores necessary involves minerals which are complex substances in real life. The first experimental work necessary, therefore, is leaching tests. (Unless pre-concentration technology such as floatation is thought to be appropriate. That would also require experimental work and the concentrate could be the feed to a hydrometallurgical circuit.) Once information on the leaching behavior of the envisaged feed is available, the calculations become meaningful.

In the second example, the liquid content of the final consolidated tailings impacts strongly on the overall reagent consumption. In this case, work on the solid-liquid separation characteristics of the leached slurry would be as important as the work necessary to measure the leaching characteristics.

As a rule of thumb, unit operations such as precipitation and ion exchange are a lot more amenable to sensible calculation without experimental data than are calculations involving leaching and solid-liquid separation.

Doing calculations of this nature contributes substantially to the understanding of a circuit under consideration. If the potential economics seem to be favorable, it



becomes a lot easier to commit the appropriate resources to the necessary experimental work. If the economics appeared to be unfavorable, the logical thing to do is re-examine the input assumptions in light of the calculations, revise unrealistic assumptions, possibly refine selected assumptions, then repeat the calculations - which should be very quick and easy if the spreadsheet was constructed properly. If the calculations still show unfavorable results, there is not much point in doing experimental work or even undertaking any more rigorous process modeling for that particular circuit. Rather move to another circuit or another opportunity entirely.

The spreadsheet-based approach illustrated in this paper does need a few simplifying assumptions, but it does not require the acquisition and associated learning curve of specialized software and it does generate useful results. It can also be done in considerably less time than is generally taken for the building of a process model, particularly if the model is being built by a novice. Done with due care, the spreadsheet-based approach can be very effective. Once built, the spreadsheet becomes a valuable tool for calculating the impact of various assumptions on things like the potential viability of the circuit in question, planning experimental work, evaluating changes, etc.

The computers of today are extremely powerful and freely available. Harnessing computation in the service of process development is a logical development in the ongoing push for higher efficiencies, lower costs, shorter timelines and generally better business decisions in the development of new mining operations.

