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Dissolution of Sludges Containing Uranium Dioxide and Metallic Uranium in Nitric Acid

T. A. Flament/A. C. Nevers

Numatec Hanford, Inc., Richland, WA 99352

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Abstract: The dissolution in nitric acid of sludges containing uranium oxide and uranium has been modeled. That study has shown that it was necessary to continuously feed the dissolver to have an appropriate control of the reaction. If a unique procedure is deemed preferable, NHO_3 6M has been used.

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78182 ST QUENTIN YVELINES CEDEX
FRANCE
Tél. + 33 1 39 48 50 00 - Télex 698316F
Fax : + 33 1 39 48 60 61

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78182 ST QUENTIN YVELINES CEDEX
FRANCE
Tél. + 33 1 39 48 50 00 - Télex 69831GF
Fax : + 33 1 39 48 60 61

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1. OBJECT

NHC is in charge of the treatment of sludges containing mainly uranium dioxide and metallic uranium.

The process is based on the following processing steps :

- a dissolution step to oxidise the pyrophoric materials ($U, UH_3, \dots$) and to dissolve radionuclides (uranium, plutonium, americium and fission products),
- a solid/liquid separation to get rid of insoluble solids (to be disposed at ERDF),
- an adjustment of the acid liquor with neutronic poisons,
- a neutralization of the acid liquor with caustic soda.

The present study concerns modeling of the dissolution step and aims to :

- compare various dissolution operating conditions, in order to help choosing the most appropriate process options (batch/continuous, acidity...), considering several scenarii (UO_2 sludges or mixed UO_2/U sludges, various particle size distributions),
- estimate NO_x flows generated during dissolution, in order to be able to design NO_x treatment equipment.

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2. KNOW HOW OF SGN RELATIVE TO DISSOLUTION MODELING

A dynamic model of semi-continuous nitric dissolution of irradiated fuels containing uranium dioxide has been developed by SGN, based on its industrial experience. Indeed, nitric dissolution is a well-known process in SGN :

- batch dissolution of fuels containing metallic uranium was operated on UP1 plant (COGEMA Marcoule, France) and UP2 plant (La Hague, France),
- batch dissolution of fuels containing uranium dioxide has been operated on UP2-400 plant (COGEMA La Hague, France), Eurochemic (Belgium) and Tokai-Mura (Japan),
- semi-continuous dissolution of fuels containing uranium dioxide has been operated on UP3 and UP2-800 plants (COGEMA La Hague, France) and has been designed for Rokkasho-Mura (Japan).

The model of dissolution developed by SGN has been qualified for La Hague plants. This model has been developed using SPEEDUP software. The main phenomena which are taken into account are the following ones :

- dissolution of uranium dioxide UO_2 , plutonium dioxide PuO_2 and fission products oxides contained in the irradiated fuel rods,
- kinetics of dissolution,
- thermodynamic liquid-vapor equilibrium,
- NO_x recombination in the dissolver head,
- mass and enthalpy balances.

Two dissolution phenomena are modeled :

- dissolution of fuel contained in zircalloy cladding,
- dissolution of fuel which got out of the zircalloy cladding : this fuel is considered in the form of spheres (diameter about 400 μm).

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The main assumptions of the model are :

- the chemical dissolution reactions are supposed to be the limiting phenomenon : no mass transfer is taken into account,
- the dissolver is perfectly stirred,
- dissolution is supposed to be total.

The kinetic law used in the model (which corresponds to the first kinetic law presented in § 4.4) was determined for irradiated PWR fuel dissolution, in nitric acidities from 2.5 to 3.5 N, for dissolved uranium concentration from 250 to 350 g/l and for temperature ranging from 70°C to boiling.

The model represents several steps of the treatment of irradiated fuel rods, which are illustrated in Appendix 3. The main steps are :

- shearing of fuel rods,
- dissolution in the dissolver basket where sheared hulls are received,
- iodine desorption from dissolved solution.

This model has been validated thanks to experimental values (liquid level, density and temperature of solution in the dissolver) measured directly on La Hague plants : therefore, the model is qualified for the operating conditions of La Hague plants (see graphs in appendix 4).

This model is the basis on which the model relative to dissolution of Hanford sludges has been built.

Nota :

As a preliminary step, it is necessary to study dissolution kinetics of UO_2 and U as the values used in SGN are specific :

- UO_2 : the kinetic law used in the model was validated for irradiated fuel rods, which is different from Hanford powder,
- U : the values available in SGN are relative to dissolution of U-Mo fuels. As detailed in §5.3.4, Mo has a huge influence on dissolution rate.

Therefore, §4 and §5 deal with dissolution kinetics of UO_2 and U.

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3. BASIC DATA

3.1. SCENARI

Four scenarii are studied. These scenarii [20] are defined by the composition of the sludges and by the diameter of the particles.

Scenario 1 :

Sludges are only composed of UO_2 . Diameter is equal to 10 μm .

Scenario 2 :

Sludges are composed of 50 % (mass) of UO_2 and of 50 % (mass) of U. Diameter is equal to 10 μm .

Scenario 3 :

Sludges are composed of 50 % (mass) of UO_2 whose diameter is equal to 10 μm and of 50 % (mass) of U whose diameter is equal to 6 mm.

Scenario 4 :

Sludges are composed of 50 % (mass) of UO_2 whose diameter is equal to 10 μm and of 50 % (mass) of U whose diameter is equal to 500 μm .

Initial specific surface area is precised in the table below for each scenario :

Scenario	Characteristics of the sludges	Specific surface area of UO_2 (m^2/g)	Specific surface area of U (m^2/g)
1	UO_2 (diameter = 10 μm)	0.055	-
2	UO_2 (diameter = 10 μm) U (diameter = 10 μm)	0.055	0.031
3	UO_2 (diameter = 10 μm) U (diameter = 6 mm)	0.055	$5.25 \cdot 10^{-5}$
4	UO_2 (diameter = 10 μm) U (diameter = 500 μm)	0.055	$6.3 \cdot 10^{-4}$

table 1

Initial specific surface area (m^2/g) of powder in the different studied scenarii

Nota :

Specific surface area designates the apparent (macroscopic) surface area of sludges particles without taking into account pores and cracks of sludges particles. So, specific surface area of sludges are different from real specific surface area (usely measured by BET method).

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3.2. ASSUMPTIONS

Assumptions have been made to estimate the following values :

- Evaporation rate is estimated to 25 kg/h. This value is proportional to the dissolver useful volume and the proportionality factor is evaluated from La Hague dissolver [16].
- A fraction of the evaporated flow is condensed in the dissolver head. This fraction is estimated to 20% (mass). So, steam flowrate from the dissolver head is equal to 20 kg/h.
- A fraction of the nitrous vapors flow reacts in the dissolver head to produce nitric acid. This fraction is estimated to 20% (mass).
- Recombined nitric acid flowrates from both the condenser and the NOx treatment are not taken into account in the nitric acid feeding flowrate.

3.3. OPERATING CONDITIONS

Simulated operating conditions are described below for batch, continuous and mixed dissolution :

1. For batch dissolution operation :

Sludges (160 kg on a dry basis) are first introduced with water (12% of dry solids). Nitric acid (12N) is added to get an average acidity of 0.5N. The dissolver is heated up to boiling. Initial volume of the solution in the dissolver can be calculated from these data (see appendix 6) : this volume (at 0.5 N) is about 1240 l.

• *Acidity :*

Acidity in the dissolver is controlled to 0.5N when heating to 100°C. Then, acidity is controlled at a constant value from 0.5 N to 2 N.

• *Heating rate :*

Reaching boiling temperature of 100 °C is realised in one hour heating or in two hours heating.

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2. For continuous dissolution operation :

- *Temperature :*
Temperature is constant and equal to 100°C during dissolution.
- *Inlet mass flowrate of sludges :*
Inlet mass flowrate of sludges in the dissolver is equal to 20 or 40 kg/h, which is related to a dissolution time of respectively 8 or 4 hours for 160 kg of sludges.
- *Acidity :*
Acidity in the dissolver is controlled at a constant value ranging from 2 to 12N.

3. For mixed dissolution operation which is a continuous dissolution followed by a batch dissolution operation :

- *Continuous dissolution :*
Continuous dissolution is performed at 100°C and at 2N. This operation lasts 8 hours (which corresponds to an inlet flowrate of sludges of 20 kg/h).
- *Batch dissolution :*
Batch dissolution is performed at 100°C and in nitric acid solution whose normality ranges from 2.25 N to 8 N.

Process requirements are :

- Boiling temperature is chosen in order to dissolve impurities present in the sludges (aluminium oxides, ferrous oxides, silica...). Moreover, dissolution at boiling temperature is preferable in order to prevent from a thermal runaway.
- After dissolution, dissolution solution is neutralized with caustic soda. Therefore, it is preferable to work with moderate acidities in order to limit the caustic soda volume for subsequent neutralization : a maximum acidity of 8 N is chosen.

Whatever the kind of dissolution operation, an air flux is introduced in the dissolver head in order to recombine nitrous vapors (thanks to oxygen in the air flux). This air flowrate is calculated in [13].

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4. DISSOLUTION OF URANIUM DIOXIDE

Dissolution of UO_2 in nitric acid solutions is an oxidizing reaction of U (+IV) to U (+VI). Dissolution reaction produces nitrate $\text{UO}_2(\text{NO}_3)_2$, nitrous vapors (NO , NO_2) and water, and consumes nitric acid.

4.1. DISSOLUTION REACTION OF UO_2

Stoichiometry of the dissolution reaction of UO_2 depends on the acidity of the solution [13]. For an acidity smaller than 3N, the stoichiometry of the reaction is :

For an acidity greater than 6N, the stoichiometry of the reaction is :

For an acidity smaller than 6N and greater than 3N, the stoichiometry of the reaction is :

with $0 < x < 1$.

No rigorous law exists for determination of x. Therefore, an interpolation is performed which gives the following equation :

$$x = \frac{\text{th}[\text{sh}(66.6 \times (x_{\text{HNO}_3} - 0.09))]}{2} + 0.5$$

where x_{HNO_3} represents the molar fraction of nitric acid in the dissolver, th and sh are respectively hyperbolic tangent and sine.

For an acidity smaller than 3N, the expression gives $x = 0$.

For an acidity greater than 6N, the expression gives $x = 1$.

Nota :

Expression of x is a complicated expression but it fits well to modeling approach.

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4.2. ENTHALPY OF REACTION

Dissolution of UO_2 is an exothermic reaction. As stoichiometry of dissolution reaction depends on acidity, enthalpy of reaction also depends on acidity.

For an acidity smaller than 3N, enthalpy of reaction is equal to $\Delta H_r = -483 \text{ kJ / kg of } \text{UO}_2 \text{ at } T = 25^\circ\text{C}$

For an acidity greater than 6N, enthalpy of reaction is equal to :

$$\Delta H_r = -301.1 \text{ kJ / kg of } \text{UO}_2 \text{ at } T = 25^\circ\text{C}$$

For an acidity smaller than 6N and greater than 3N, enthalpy of reaction is expressed as a function of the stoichiometric factor x depending on acidity :

$$\Delta H_r = (181.9 \times x - 483) \text{ kJ / kg of } \text{UO}_2 \text{ at } T = 25^\circ\text{C}$$

Calculation of x is given in § 4.1.

4.3. GENERAL ASPECTS ON DISSOLUTION OF UO_2 : LITERATURE SURVEY

In this paragraph, some parameters of dissolution of UO_2 are studied, in order to determine their influence on dissolution kinetics.

4.3.1. Influence of acidity on dissolution kinetics

Influence of acidity on dissolution rate may be highlighted on the following graph on which fraction of dissolved UO_2 is plotted versus time.

graph 1

Dissolution kinetics for non irradiated (—) UO_2 and (---) U_3O_8 powders at 95°C in a stirred nitric acid solution at constant acidity from 0.3N to 2N [3]

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Nota :

It is to be noted that particle size distribution (and therefore specific surface area) has a huge influence on dissolution time. Real specific surface area of UO_2 powder is $1.8 \text{ m}^2/\text{g}$ in [3] (see graph 1), which is higher than the one of Hanford sludges in the different scenarii. In order to compare, specific areas of sludges are precised in the table 1 (see § 3.1).

For a low acidity, initial dissolution rate is very slow, which corresponds to an induction period. This period corresponds to the necessary time to produce nitrous acid which acts as a catalyst for the dissolution reaction. For instance, this period lasts 30 minutes at 0.3N and 20 minutes at 0.6N.

For an acidity greater than 1N, no induction period exists anymore.

If acidity is high enough ($> 1\text{N}$), all dioxide uranium is dissolved within a short time. Powders may not be totally dissolved in a reasonable time if acidity is too small.

4.3.2. Influence of temperature on dissolution kinetics

Assuming constant acidity, dissolution rate constant k_T is calculated at T with an Arrhenius law :

$$k_T = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

with :

- k_T : rate constant (independent on acidity) ($\text{min}^{-1}(\text{mol/l})^{-a}$)
- k_0 : rate constant (independent on acidity and temperature) ($\text{min}^{-1}(\text{mol/l})^{-a}$)
- E_a : energy of activation (J/mol)
- R : constant for ideal gases ($R = 8.314 \text{ J/K/mol}$)
- T : temperature (K)

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4.3.3 Influence of stirring on dissolution kinetics

Experiments [3] show that stirring of dissolution solution decreases dissolution rate. Dissolution of UO_2 is catalyzed by nitrous acid HNO_2 which is a reduction product of HNO_3 . Stirring causes a decrease of nitrous acid concentration at the solid surface. As a consequence, dissolution rate decreases.

However, high stirring efficiency (stirring speed exceeding 500 rpm in [3]) has no more effects on dissolution rate in the experimental conditions (temperature from 30 to 95°C, nitric acid from 0.3 to 10N in [3]).

[11] reports dissolution rates ($\text{mg}/\text{cm}^2/\text{min}$) of the same non irradiated UO_2 pellets in nitric acid solutions with and without mechanical stirring. Generally, rates obtained in agitated solutions are seven times smaller at 8N, and 5 times smaller at 6N than the ones obtained in non agitated solutions.

acidity (N)	T = 95°C		T = 80°C	
	no agitation	agitation	no agitation	agitation
8	3.5	0.5	1.5	0.2
6	1.5	0.3	0.70	0.15

table 2

Dissolution rate ($\text{mg}/\text{cm}^2/\text{min}$) of unirradiated pellets of UO_2 in nitric acid solutions (6 and 8 N) with and without mechanical stirring [11]

It is worth noticing that operating dissolution at boiling temperature may induce stirring of the solution due to gas bubbles formation, which increases while heating rate increases. Quantitative influence of such stirring action is difficult to evaluate.

4.4. KINETIC LAWS STUDIED

Three different kinetic laws for the dissolution of UO_2 have been studied.

4.4.1. Initial kinetic law in the model previously developed by SGN for La Hague plant

This first kinetic law is based on the Arrhenius law and depends on the acidity and the concentration of dissolved uranium.

This law applies in the range of acidity from 2.5 to 3.5N, the range of uranium concentration from 250 to 350 gU/l, and the range of temperature from 70°C to boiling, this law was determined for irradiated fuels [14].

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The expression is :

$$V = k_0 \exp\left(\frac{-E_a}{RT}\right) ([H^+] + [U])^2$$

with :

V	: dissolution rate (mg/cm ² /min)
k ₀	: rate constant (mg/cm ² /min)/(mol/l) ²
E _a	: energy of activation (J/mol)
[H ⁺]	: molar concentration of nitric acid (mol/l)
[U]	: molar concentration of dissolved uranium (mol/l)
R	: constant for ideal gases (R=8.314 J/mol/K)

The values of k₀ and E_a were determined for fuels [4] :

E _a	=	4.35 kcal/mol = 18183 J/mol
k ₀	=	11681 (mg/cm ² /min)/(mol/l) ²

Nota :

Though this kinetic law has been developed for uranium concentration ranging from 250 to 350 gU/l, this law is supposed to be still applicable to our case in which complete dissolution of 160 kg of uranium dioxide in the dissolver will lead to approximately 100 gU/l.

4.4.2. Second kinetic law

Determination of kinetic law based on experimental measurements is detailed in appendix 1. The expression, which is assumed to be the same as in §4.4.1, is precised below :

$$V = k_0 \exp\left(\frac{-E_a}{RT}\right) ([H^+] + [U])^2$$

with :

V	: dissolution rate (mg/cm ² /min)
k ₀	: rate constant (mg/cm ² /min)/(mol/l) ²
E _a	: energy of activation (J/mol)
[H ⁺]	: molar concentration of nitric acid (mol/l)
[U]	: molar concentration of dissolved uranium (mol/l)
R	: constant for ideal gases (R=8.314 J/mol/K)

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The value of k_0 was determined on the basis of experimental dissolution of non irradiated UO_2 powder whose particle size distribution was known [1], assuming the same value for E_a as in §4.4.1 :

$$\begin{aligned} E_a &= 4.35 \text{ kcal/mol} = 18183 \text{ J/mol} \\ k_0 &= 14.53 \text{ (mg/cm}^2\text{/min)/(mol/l)}^2 \end{aligned}$$

4.4.3. Third kinetic law

The third one is determined according to experimental measurements ([2] and [3]) on non irradiated powder. Experiments are carried out in stirred solutions. This law depends on acidity, temperature and dissolved fraction. The law has been validated for a temperature range of 30-95°C and acid concentration range of 0.3-10 N. The rate equation is :

$$1 - (1-X)^{1/3} = k \cdot t$$

with

X	: fraction of dissolved uranium
k	: apparent rate constant (min) ⁻¹
t	: time (min)

with an apparent rate constant depending both on acidity and temperature as following :

$$k = k_1 [\text{H}^+]^a \exp\left(-\frac{E_a}{RT}\right)$$

with :

a	: degree of dependence on acidity (a=1.7)
k	: apparent rate constant (min ⁻¹)
k_1	: rate constant (min ⁻¹ (mol/l) ^{-a})
E_a	: energy of activation (J/mol)
$[\text{H}^+]$	: molar concentration of nitric acid (mol/l)
T	: temperature (K)
R	: constant for ideal gases (R=8.314 J/mol/K)

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The differential expression of the kinetic rate, assuming that acidity and temperature are constant (k constant), is :

$$V' = 3 \cdot k \cdot \left(\frac{m(t)}{m_0} \right)^{2/3} \cdot m_0$$

with :

V' : dissolution rate (mg/min)
 $m(t)$: dissolved uranium mass (mg)
 m_0 : initial mass of uranium (mg)

Calculations to obtain the differential form of the kinetic law are detailed in appendix 2.

The numerical values for acid concentration of 1 to 2 N and at 95°C are :

E_a = 20.5 kcal/mol = 85690 J/mol
 k_1 = $9.3 \cdot 10^{10} \text{ min}^{-1} (\text{mol/l})^{-1.7}$
 a = 1.7

N.B. : This law gives a dissolved fraction, whose literal expression is independent of the specific surface area of the powder. It must be noted that the law was determined for UO_2 powder with an apparent specific surface area of $0.14 \text{ m}^2/\text{g}$. A proportionality factor is introduced to estimate the dissolution rate for our specific sludges whose apparent specific surface area (see §3.1) is about $0.06 \text{ m}^2/\text{g}$ (supposing the same ratio real specific surface area/apparent specific surface area) :

$$V = V' \times \frac{0.06}{0.14}$$

with

V : dissolution rate (mg/min) adapted to Hanford UO_2 sludges.

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5. DISSOLUTION OF METALLIC URANIUM

Dissolution of metallic uranium has been less studied than dissolution of UO_2 . Dissolution of metallic uranium is a vigorous, sometimes explosive reaction in HNO_3 when uranium is finely divided. On the contrary, dissolution of a metallic mass of uranium occurs at much more moderate rates (See § 5.3).

5.1. REACTION OF DISSOLUTION OF METALLIC U

The stoichiometry of the dissolution reaction of U in nitric acid depends on acidity [19]. For an acidity smaller than 6N, the stoichiometry of the reaction is :

For an acidity greater than 8N, the stoichiometry of the reaction is :

For an acidity greater than 6N and smaller than 8N, the stoichiometry of the reaction is :

with $0 \leq x' \leq 1$.

For an acidity smaller than 6N, $x' = 0$.

For an acidity greater than 8N, $x' = 1$.

It is to be noted that whatever the acidity, dissolution of U produces more nitrous fumes than dissolution of UO_2 .

Table 3 presents a summary of the stoichiometric factors of NO and NO_2 produced by both dissolution of U and UO_2 at different acidities :

Acidity	$[\text{H}^+] < 3 \text{ N}$	$3 \text{ N} < [\text{H}^+] < 6 \text{ N}$	$6 \text{ N} < [\text{H}^+] < 8 \text{ N}$	$8 \text{ N} < [\text{H}^+]$
Dissolution of UO_2	$2/3 \text{ NO}$	$2/3 (1-x) \text{ NO} + (2x) \text{ NO}_2$	2 NO_2	2 NO_2
Dissolution of U	2 NO	2 NO	$2 (1-x') \text{ NO} + (6x') \text{ NO}_2$	6 NO_2

table 3

Stoichiometric factors of NO and NO_2 produced by both dissolution of U and UO_2 at different acidities

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5.2. ENTHALPY OF REACTION

Dissolution of metallic U is an exothermic reaction. The enthalpy of dissolution reaction of U is approximately ten times the one of dissolution reaction of uranium dioxide UO_2 .

As stoichiometry of dissolution reaction depends on acidity, enthalpy of reaction also depends on acidity.

For an acidity smaller than 6N, enthalpy of reaction is equal to :

$$\Delta H_r = -4520 \text{ kJ / kg of U at } T = 25^\circ\text{C}$$

For an acidity greater than 8N, enthalpy of reaction is equal to :

$$\Delta H_r = -3883 \text{ kJ / kg of U at } T = 25^\circ\text{C}$$

For an acidity smaller than 8N and greater than 6N, enthalpy of reaction is written as a function of the stoichiometric factor x' depending on acidity :

$$\Delta H_r = (-4520 - 637 \times x') \text{ kJ / kg of U at } T = 25^\circ\text{C}$$

5.3. GENERAL ASPECTS ON DISSOLUTION OF U : LITERATURE SURVEY

5.3.1. Influence of shape, size, density of U samples

Dissolution of metallic uranium is an anisotropic reaction. So, the shape of the metal sample has an influence on dissolution rate.

Some experiments made on pie shaped wedges (1.27 cm thick and radius equal to 2.54 cm) show that initial dissolution rate was four times faster on the top and bottom than on the sides of the pie shaped wedges in nitric acid 8 N at 25°C .

Reference [7] reports that dissolution rate is smaller on the rolled rod surface than in the core.

The rate for samples cut from a rolled rod increased as the fraction of the total surface area perpendicular to the axis of the rod was increased [6], so dissolution rate is often expressed as rod length per unit of time. Value given in [9] is 0.175 mm/h for empty rods of irradiated uranium (external diameter = 9.5 cm; internal diameter = 7.7 cm; length = 34 cm) dissolved in nitric acid 6.5 N at boiling temperature. In nitric acid 6 N at boiling temperature, [10] gives 0.16 mm/h for metallic U (density mentioned : 19 g/cm³).

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Real specific surface area, related to density, has a great effect on dissolution rate. [6] reports that samples with small grain sizes (due to metallurgical treatment of rolling) dissolve quickly. Values of initial dissolution rates are given in the table with the corresponding density of U samples (temperature and acidity are not mentioned).

Density (g/cm ³)	Initial dissolution rates (mg/cm ² /h)
18.88	0.65
18.90	0.50
19.04	0.13

table 4
Initial dissolution rates of different density U samples [6]

5.3.2. Influence of stirring on dissolution

Experiments [6] show that stirring decreases dissolution rate. Similar explanations as those reported for UO_2 are given. [6] reports that after 90 hours in concentrated HNO_3 at 0°C, the average dissolution rate of a rod of U (4.06 cm diameter) was nearly eight times greater than that of a similar rod in a solution stirred at 360 rpm.

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5.3.3. Influence of nitrate concentration on dissolution

Nitrate concentration affects dissolution rate. Graph 2 shows that dissolution rate is affected by uranyl nitrate concentration at boiling temperature whatever the acidity is.

graph 2

Dissolution rate of metallic uranium versus nitric acid and uranyl nitrate concentrations.
Uranyl concentrations : (A) 0.0 M; (B) 0.5 M; (C) 1.0M [10]

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Dissolution kinetics is not only improved by presence of uranyl nitrate, but also by all forms of nitrates in the solution, such as undissociated HNO_3 , and free nitrate concentration.

[7] concludes that the kinetic law of metallic U dissolution in uranyl nitrate and nitric acid solutions is proportional to the total nitrate concentration raised to an exponent, which is equal to 2.6 as it is shown on the following graph :

graph 3

Dependence of uranium dissolution rate versus nitrate concentration [7]

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5.3.4. Influence of impurities (Mo)

Literature survey shows that alloys containing uranium and molybdenum dissolve quicker than pure metallic U in the same operating conditions.

[8] gives some values of dissolution rate of metallic uranium rods in nitric acid 3 N at boiling temperature :

Initial rod size (d diameter and L length) (cm)	Characteristics of the rods	Dissolution rate (mg/cm ² /min)
d = 2.6 L = 10	Full rods U - Mo (1%) alloy	33
d = 1.4 L = 54	Annular rods U - Mo (0.5%) alloy	30

table 5

Dissolution rates of samples of U-Mo alloys rods [8]

The same order of magnitude is given in [17] in which dissolution rates of full rods of U-Mo (0.5 - 1% Mo) alloys are equal to about 35 mg/cm²/min. In order to make a comparison, the dissolution rate of pure metallic U rods in nitric acid solution (acidity ranging from 3 to 4 N) is measured to 5 mg/cm²/min [9].

Nota :

It is reported in [17] and in [18] that precipitation of molybdenic compounds may happen in concentrated and acid solutions, so one must be careful if adding Mo.

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5.4. KINETIC LAW STUDIED

The kinetic law studied has been determined for a range of HNO_3 concentration from 3 to 8 N. No range of uranium concentration is precised. This law was determined for non irradiated as-fabricated N-reactor fuel uranium [7].

The expression of the kinetic law is :

$$V = k_0 \exp\left(-\frac{E_a}{RT}\right) ([\text{H}^+] + 2[\text{U}])^{2.6}$$

with :

- V : dissolution rate of U per unit of area (mg/min/cm²)
- k_0 : rate constant (mg/min/cm²)/(mol/l)^{2.6}
- E_a : energy of activation (J/mol)
- $[\text{H}^+]$: molar concentration of nitric acid (mol/l)
- $[\text{U}]$: molar concentration of dissolved uranium (mol/l)
- R : constant for ideal gases (R=8.314 J/mol/K)

Assuming that dependence of k_0 on temperature is negligible, the value of k_0 is determined [2] :

$$k_0 = 1,853 \cdot 10^5 \text{ (mg / min / cm}^2\text{) / (mol / l)}^{2.6} \quad (\text{value determined at } 103^\circ\text{C})$$

Assuming that dependences of E_a on both temperature and acidity are negligible, the value of the energy of activation is [2] :

$$E_a = 45980 \text{ J / mol} \quad (\text{determined for } 71^\circ\text{C} \leq T \leq 105^\circ\text{C and for } \text{HNO}_3 \text{ 7.8 N})$$

Nota :

In order to compare with literature values (see §5.3.4), dissolution rate of metallic uranium in nitric acid 4.2 N at 100°C, calculated with this kinetic law, is equal to 2.8 mg/cm²/min.

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6. MODELING

The developed model is relative to batch dissolution. Continuous dissolution has been calculated in a simple way without modeling. The main modifications of the initial model (presented in §2) are :

- adaptation to batch dissolution,
- addition of metallic uranium dissolution,
- choice of adapted dissolution kinetics (UO_2 and U).

The model has been developed using SPEEDUP software (version 5.6). This chapter describes the model and presents the assumptions and the equations of the model.

6.1. DESCRIPTION OF THE MODEL

The developed model represents the system drawn below :

graph 4: Modeled system

Nota : C stands for controller

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The dissolution of sludges in nitric acid occurs in the vessel. The following phenomena are modeled :

- dissolution of UO_2 and U sludges (kinetics, generated power, generated species)
- evaporation,
- partial condensation in the dissolver head,
- partial NO_x recombination in the dissolver head.

Acid concentration in the dissolver is kept constant during dissolution. Therefore, the model includes a controller which regulates acid concentration by action on the nitric acid feed flowrate.

6.2. ASSUMPTIONS

The dissolver is supposed to be perfectly stirred.

Dissolution of UO_2 and U particles is assumed to be chemically rate controlled (no diffusion limitation).

Dissolution of particles is supposed to be kinetically uniform on the whole apparent surface area of particles.

Though apparent surface area of particles decreases while attacked by nitric acid, the total real surface area of the sludges particles increases at the beginning [6]. As it is difficult to calculate the roughness increase of particles during the dissolution, kinetic rates are calculated considering the apparent surface area of particles instead of the total real surface area of particles.

Sludges are assumed to be spherical particles.

Sludges are considered as pure UO_2 and U. Other compounds are neglected.

Taking into account the low acidity of dissolution solutions in most cases, evaporation of nitric acid is neglected.

Variations of enthalpy reactions between 25 and 100°C is neglected.

Dissolution is supposed to be total.

Induction time is not modeled.

Influence of stirring (through boiling) is not taken into account.

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6.3. MAIN EQUATIONS OF THE MODEL

6.3.1. Dissolver

6.3.1.1. Mass balances

For each compound listed above, the expression of the mass balance sheet is :

- for water and nitric acid :

$$Q_i^e = Q_i^s - Q_i^R + E_i + \frac{d(Acc_i)}{dt}$$

- for uranyl nitrate :

$$Q_i^e = Q_i^s - Q_i^R + \frac{d(Acc_i)}{dt}$$

with :

E_i : mass evaporation flux of compound i (kg/h)

Q_i^e : inlet mass flowrate of compound i (kg/h)

Q_i^s : outlet mass flowrate of compound i (kg/h)

Q_i^R : mass reacting flow rate (kg/h)

$Q_i^R > 0$ for a product,

$Q_i^R < 0$ for a reactant,

Acc_i : mass accumulation of compound i in the vessel (kg)

t : time (h)

Mass concentrations of compounds i are calculated, with the following expression :

$$C(i) = \frac{Acc(i)}{V}$$

with :

$Acc(i)$: mass accumulation of compound i in the vessel (kg)

$C(i)$: mass concentration of compound i (kg/m³)

V : volume of liquid in the vessel (m³)

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- for uranium dioxide and metallic uranium :

Mass flowrates of dissolved U and UO_2 are expressed as :

$$Q_i^D = - \frac{d(\text{Acc}_i)}{dt} \quad ;$$

with :

Q_i^D : mass flux of dissolved compound i (U, UO_2) (kg/h)
 Acc_i : mass accumulation of compound i in the vessel (kg)
 t : time (h)

- for NO and NO_2 :

$$Q_i^I = Q_i^R \text{ (gaseous holdup is neglected)}$$

with :

Q_i^I : outlet mass flowrate of compound i (kg/h)
 Q_i^R : mass reacting flowrate (kg/h)
 $Q_i^R > 0$ for a product,
 $Q_i^R < 0$ for a reactant.

6.3.1.2. Determination of reaction flowrates

Dissolution of uranium dioxide and metallic U produces water, uranyl nitrate and NO_x and consumes nitric acid.

a Flowrates of dissolved U and UO_2

Powders of U and UO_2 are composed of identical spherical particles whose diameter decreases during dissolution. Flowrates of dissolved U and UO_2 are expressed as :

$$Q_i^D = 4\pi R_i^2 \times N_i^{\text{sph}} \times 60 \times V_i \times 10^{-3}$$

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with :

- R_i : radius of spherical particles of compound i (cm)
 N_i^{sph} : number of spherical particles of compound i (constant)
 V_i : dissolution rate of compound i (mg/cm²/min)
 Q_i^D : mass dissolved flux of compound i (U, UO₂) (kg/h)

Total number of spherical particles is constant and calculated with :

$$N_{tot}^{sph} = N_U^{sph} + N_{UO_2}^{sph}$$

with :

- $N_U^{sph}, N_{UO_2}^{sph}$: number of spherical particles of compound i (U, UO₂) (constant)
 N_{tot}^{sph} : total number of spherical particles

b Flowrate of reacting nitric acid

According to the stoichiometry of UO₂ and U dissolution reactions (See §4.1 and §5.1), mass flux of reacting nitric acid is equal to :

$$Q_{HNO_3}^R = -M_{HNO_3} \left[\frac{4}{3} (2+x) \frac{Q_{UO_2}^D}{M_{UO_2}} + 4(1+x') \frac{Q_U^D}{M_U} \right]$$

Nomenclature is explained in § e.

c Flowrate of water

According to the stoichiometry of UO₂ and U dissolution reactions (See §4.1 and §5.1), mass flux of produced water is equal to :

$$Q_{H_2O}^R = M_{H_2O} \left[\frac{2}{3} (2+x) \frac{Q_{UO_2}^D}{M_{UO_2}} + 2(1+x') \frac{Q_U^D}{M_U} \right]$$

Nomenclature is explained in § e.

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d Flowrate of uranyl nitrate

According to the stoichiometry of UO_2 and U dissolution reactions (See §4.1 and §5.1), mass flux of produced uranyl nitrate is equal to :

$$Q_{\text{UO}_2(\text{NO}_3)_2}^R = M_{\text{UO}_2(\text{NO}_3)_2} \left[\frac{Q_{\text{UO}_2}^D}{M_{\text{UO}_2}} + \frac{Q_U^D}{M_U} \right]$$

Nomenclature is explained in § e.

e Flowrates of nitrous vapors

Nitrous vapors which are generated in the dissolver are NO and NO_2 .

According to stoichiometries of UO_2 and U dissolution reactions (See §4.1 and §5.1), mass flux of NO is equal to :

$$Q_{\text{NO}}^R = M_{\text{NO}} \left[\frac{2}{3} (1-x) \frac{Q_{\text{UO}_2}^D}{M_{\text{UO}_2}} + 2(1-x') \frac{Q_U^D}{M_U} \right]$$

According to stoichiometries of UO_2 and U dissolution reactions (See §4.1 and §5.1), mass flux of NO_2 is equal to :

$$Q_{\text{NO}_2}^R = M_{\text{NO}_2} \left[2x \frac{Q_{\text{UO}_2}^D}{M_{\text{UO}_2}} + 6x' \frac{Q_U^D}{M_U} \right]$$

with :

- Q_i^D : dissolved mass flow rate of compound i (kg/h)
- Q_i^R : mass reactional flux of compound i in the vessel (kg/h)
 - $Q_i^R > 0$ if compound i is a product,
 - $Q_i^R < 0$ if compound i is a reactant,
- M_i : molar mass of compound i (g/mol)
- x, x' : stoichiometric factors, depending on the acidity of the solution, for the dissolution of UO_2 and U.

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6.3.1.3 Determination of density

a. Dissolution solution

The density of the liquid in the vessel at the temperature T is evaluated on the basis of the density at 25°C.

The expression of the density at the temperature T is :

$$d(T) = d(25^{\circ}\text{C}) \cdot (1.0125 - 0.0005 \cdot T) + 0.000145 \cdot T - 0.003625$$

with :

T : temperature of the liquid in the vessel (°C)

d(T) : density at temperature T (kg/m³)

d(25°C) : density at 25°C (kg/m³)

The density at 25°C is calculated with the following expression :

$$d(25^{\circ}\text{C}) = 1.0012 + 0.03096 [\text{H}^+] + 0.3177 [\text{U}]$$

with :

[H⁺] : molar concentration of nitric acid (mol/l)

[U] : molar concentration of uranium (mol/l)

b. Nitric acid

Density of nitric acid feed is a function of temperature and acidity of the feed :

$$d_{\text{acid}} = (1.0125 - 0.0005 \cdot T) f(N) + 0.145 \cdot T - 3.6$$

with

T : temperature of the nitric acid feed (°C)

N : acidity of the nitric acid feed (mol/l)

f(N) : density at 25°C dependent of normality (kg/m³)

d_{acid} : density (kg/m³)

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6.3.1.4. Dissolution heat

Power produced by dissolution is calculated as a function of flow rates of dissolved uranium and uranium dioxide.

Power generated by dissolution of UO_2 is expressed as :

$$P_{\text{UO}_2} = \Delta H_r^{\text{UO}_2} \times \left(\frac{Q_{\text{UO}_2}^p}{3600} \right)$$

Specific enthalpy of dissolution of UO_2 is given in §4.2.

Power generated by dissolution of U is expressed as :

$$P_U = \Delta H_r^U \times \left(\frac{Q_U^p}{3600} \right)$$

Specific enthalpy of dissolution of U is given in §5.2.

Nomenclature is presented below :

- Q_i^p : dissolved mass flow rate of compound i (kg/h)
- ΔH_r : reaction enthalpy for dissolution of compound i (kJ/kg)
- M_i : molar mass of compound i (g/mol)
- P_i : power generated by dissolution of compound i (kW)

6.3.2. Regulation loop

Regulation of nitric acid concentration in the dissolver is performed by action on the nitric acid feed flowrate using a proportional controller.

The difference between the set point and the normality measured in the dissolver is E :

$$E = N_{\text{SP}} - N_{\text{dissolver}}$$

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with :

- N_{SP} : set point of acidity (mol/l)
 $N_{dissolver}$: acidity in the dissolver (mol/l)
 E : error between set point and acidity regulated in the dissolver (mol/l)

Equation of regulation is :

$$V_{acid} = e + G \times E$$

with :

- V_{acid} : volumetric flux of the nitric acid feed (m³/h)
 e : systematic deviation of the perfect controller (m³/h)
 G : perfect controller gain ((m³/h)/(mol/l))

6.3.3. Dissolver head

In the gaseous head upon the liquid in the dissolver, present components are water, NO, and NO₂.

Recombination reactions of nitrous vapors occur in the head following the chemical reactions given below :

First of all, NO is oxidised into NO₂

Absorption of nitrogen dioxide into water regenerates nitric acid :

Mass balance of water is expressed as (gaseous holdup is neglected) :

$$V_{H_2O}^s = (1 - \alpha_c) Q_{H_2O}^s$$

$$\alpha_c Q_{H_2O}^e = -Q_{H_2O}^R + Q_{H_2O}^i$$

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with :

$$Q_{H_2O}^R = -\frac{M_{H_2O}}{2} \left[\frac{Q_{NO}^R}{M_{NO}} + \frac{Q_{NO_2}^R}{M_{NO_2}} \right]$$

Mass balance of nitric acid is expressed as (gaseous holdup is neglected) :

$$Q_{HNO_3}^s = Q_{HNO_3}^R$$

with :

$$Q_{HNO_3}^R = M_{HNO_3} \left[\frac{Q_{NO}^R}{M_{NO}} + \frac{Q_{NO_2}^R}{M_{NO_2}} \right]$$

Mass balance of nitrogen monoxide is expressed as (gaseous holdup is neglected) :

$$Q_{NO}^e = V_{NO}^s - Q_{NO}^R$$

with :

$$Q_{NO}^R = -\alpha_r Q_{NO}^e$$

Mass balance of nitrogen dioxide is expressed as (gaseous holdup is neglected) :

$$Q_{NO_2}^e = V_{NO_2}^s - Q_{NO_2}^R$$

with :

$$Q_{NO_2}^R = -\alpha_r Q_{NO_2}^e$$

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Corresponding nomenclature is precised below :

- Q_i^g : inlet gaseous flowrate of compound i (kg/h)
- Q_i^l : outlet liquid flowrate of compound i (kg/h)
- V_i^g : outlet gaseous flowrate of compound i (kg/h)
- Q_i^R : reactional flowrate of compound i (kg/h)
- α_c : mass condensed fraction (= 0.20)
- M_i : molar mass of compound i (g/mol)
- α_r : mass recombination rate of nitrous vapors (= 0.20)

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7. PRELIMINARY SIMULATIONS : CHOICE OF A KINETIC LAW RELATIVE TO UO_2 DISSOLUTION

Preliminary simulations of scenario-1 (100% UO_2) have been performed in order to choose the most appropriate kinetic law for dissolution of UO_2 among the three different kinetic laws studied in § 4.4. These simulations have been performed considering batch dissolution.

7.1. SIMULATED OPERATING CONDITIONS

Dissolution is a batch operation.

Temperature is increased linearly and reaches 100°C (boiling) after one hour heating.

Normality is set to 0.5N while heating and is increased to 2N when temperature reaches 100°C .

As acidity is always equal to or smaller than 2N, the stoichiometry of the reaction of dissolution of UO_2 indicates that only NO is formed.

Nota 1:

Dissolution is assumed to be negligible at 0.5N when simulating dissolution with the first and third kinetic laws (to simulate induction time). This assumption is not made with the second law, as this law gives by itself a negligible dissolved fraction at 0.5N.

Nota 2:

The simulated controller is perfect : therefore, time to increase acidity from 0.5N to 2N is negligible in the simulations.

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7.2. RESULTS

Results of the simulations are presented in table 6.

	First kinetic law (See § 4.4.1)	Second kinetic law (See § 4.4.2)	Third kinetic law (See § 4.4.3)
Temperature (°C)	100°C	100°C	100°C
Acidity (N)	2N	2N	2N
Dissolution time at 100°C	6 minutes	1 hour	12 minutes
Total time (including heating)	1 h 06'	2 h 00'	1 h 12'
Maximum NOx flowrate (Nm ³ /h)	122.5	12.5	54
Dissolution rate (mg/min/cm ²) at the end of dissolution time (100°C, 2 N, ≈100 gU/l)	177	0.22	—*

table 6

Summary of the preliminary simulations

*: Actually, the third kinetic law gives a dissolution rate in mg/min.

Graphs of the results of the simulations are presented in appendix 7.

7.3. DISCUSSION

The three kinetic laws lead to very different results. The second and third kinetic laws may be more adapted to our case as they were specifically established for UO₂ powder. However it is quite difficult to conclude which kinetic law is the most adapted one without any experimental results relative to Hanford specific sludges.

For the present study, the third kinetic law is chosen because it gives average results. This choice will need to be discussed when experimental results are available.

7.4. APPLICABILITY OF KINETIC LAWS FOR UNIRRADIATED UO₂/U TO IRRADIATED UO₂/U

According to SGN experience in term of dissolution of irradiated fuels, dissolution rate of irradiated metallic uranium rod (1000 MWj/t) is estimated to be twice the one of non irradiated uranium rods [9].

In irradiated uranium rods, porous areas are more important than in rods of non irradiated uranium. So, it seems probable that irradiated uranium is characterized by a greater real specific surface area. As a result, dissolution rates (relative to apparent specific surface area) of irradiated uranium are greater than the ones of non irradiated uranium.

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Same statements are reported by Schultz (1972, cited in [7]), but no data are given. Dissolution rate of irradiated UO_2 powder is also assumed to be greater than the one of non irradiated UO_2 .

The factor between dissolution rates of irradiated matter and non irradiated matter depends in fact on the history of the previous treatments (process, irradiation level,...) and on the matter shape.

As knowledge about this factor is not clearly determined, the kinetic laws which are chosen for U and UO_2 , determined for non irradiated powders, are assumed to be applicable to slightly irradiated Hanford sludges. If experimental values are available later on, it will be interesting to reconsider this assumption.

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8. SIMULATIONS OF BATCH DISSOLUTION

Batch dissolution is studied for the scenarii 1,2 and 3.

8.1. OPERATING CONDITIONS

Dissolution is a batch operation.

Temperature is increased linearly and reaches 100°C (boiling) after one or two hours heating.

Normality is set to 0.5N while heating up to 100°C, then three cases are simulated :

- acidity is kept at 0.5N,
- acidity is increased to 1N,
- acidity is increased to 2N.

As acidity is always equal to or smaller than 2N, the stoichiometry of the reaction of dissolution of UO_2 indicates that only NO is formed.

Nota :

The simulated controller is perfect : therefore, time to increase acidity from 0.5N to 2N is negligible in the simulations.

8.2. RESULTS

Results of simulations of scenarii 1,2 and 3 are summed up in the table 7 (see page 42).
Graphs of the results of the simulations (scenarii 1 and 2) are presented in appendix 8.

	0.5N, 100°C 100°C after 2 hours heating	1N, 100°C 100°C after 1 hour heating	1N, 100°C 100°C after 2 hours heating	2N, 100°C 100°C after 1 hour heating	2N, 100°C 100°C after 2 hours heating
Scenario 1 100% UO ₂ 10μm	Max power : 26.9 kW Max NOx : 7.7 Nm ³ /h Dissolution time : 3h06'	Max power : 76.3 kW Max NOx : 21.8 Nm ³ /h Dissolution time : 1h24'	Max power : 60 kW Max NOx : 17.0 Nm ³ /h Dissolution time : 2h24'	Max power : 166.8 kW Max NOx : 47.8 Nm ³ /h Dissolution time : 1h12'	Max power : 127.2 kW Max NOx : 36.5 Nm ³ /h Dissolution time : 2h12'
Scenario 2 50% UO ₂ 10μm 50% U 10μm	Max power : 100 kW Max NOx : 13.1 Nm ³ /h Dissolution time : 3h09'	Max power : 240 kW Max NOx : 33.6 Nm ³ /h Dissolution time : 1h40'	Max power : 235 kW Max NOx : 32.9 Nm ³ /h Dissolution time : 2h40'	Max power : 620 kW Max NOx : 86.7 Nm ³ /h Dissolution time : 1h15'	Max power : 570 kW Max NOx : 79.2 Nm ³ /h Dissolution time : 2h15'
Scenario 3 50% UO ₂ 10μm 50% U 6mm	Too slow	Too slow	Too slow	Max power : 36 kW Max NOx : 10.3 Nm ³ /h Dissolution time > 60h	-

Table 7
Scenarii 1, 2 and 3 - batch dissolution

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Nota :

Some simulations have been performed at low temperatures. The results are summarized in the table below. Dissolution times are longer, but as temperatures were too low to cope with insoluble impurities, these configurations have not been considered as suitable.

Scenario	1	2
Acidity (N)	3 N	6 N
Temperature (°C)	temperature linearly increased to 40°C in 30 minutes	temperature constant and equal to 25°C
Max. Power generated (kW)	5.3	3.4
Max. NOx flux (kg/h)	-	6
Dissolution time	> 6 hours (30 kg of UO ₂ were not yet dissolved)	18 hours

table 8

Simulations (scenarii 1 and 2) at low temperatures - batch dissolution

8.3. DISCUSSION

Preliminary nota :

If possible, generated power should be kept lower than the power necessary to maintain an evaporation rate of 25 kg/h (~ 16 kW), i.e. to maintain a heating mode and to avoid switching to a cooling mode.

Small particles (10 µm) dissolve quite easily at 100°C, whatever their composition (UO₂ or U). Therefore, even with a low acidity of 0.5 N, the maximum NOx flowrate and the maximum generated power are high. From 1 N, these values become far too high and are not acceptable.

At 0.5 N and 100°C, scenarii 1 and 2 need approximately the same time to achieve complete dissolution (~ 3 hours). However, maximum NOx flowrate and generated power are much more important for a UO₂ /U mixture than for pure UO₂, as dissolution of U generates three times more NOx and eight times more power for one mole dissolved.

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On the other hand, sludges containing "big" U particles (6 mm) are very difficult to dissolve. At 2 N and 100°C, necessary time to achieve complete dissolution is greater than 60 hours. Moreover, maximum generated power (36 kW) is higher than the one necessary to maintain about an evaporation rate of 25 kg/h. Even if a greater acidity would give a smaller (and so more reasonable) dissolution time, it would give a higher maximum generated power.

Therefore, batch dissolution of sludges containing "big" U particles seems to be a problem : at low acidity, dissolution time is far too long, and at higher acidity, maximum generated power is far too high.

As a conclusion, batch dissolution does not seem to be the best solution to cope with the three studied scenarii as small particles (10 μm) dissolve too quickly and "big" U particles (6 mm) dissolve too slowly (generating however a high maximum power).

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9. SIMULATIONS OF CONTINUOUS DISSOLUTION

Continuous dissolution is studied for the scenarii 1, 2, 3 and 4.

9.1. OPERATING CONDITIONS

Dissolution is a continuous operation.

Temperature is equal to 100°C and normality is set at a constant value from 2N to 12N.

If acidity is set to 2N, stoichiometries of the reaction of dissolution of UO_2 and U indicate that only NO is produced. (See §4.1 and §5.1)

If acidity is set to 6N, stoichiometry of the reaction of dissolution of UO_2 and U show that both NO and NO_2 is produced. (See §4.1 and §5.1)

If acidity is set to 12N, stoichiometries of the reaction of dissolution of UO_2 and U indicate that only NO_2 is produced. (See §4.1 and §5.1)

Nota :

Acidities greater than recommended value of 8 N (see §3.3) have been tested in order to cope with scenario 3.

9.2. RESULTS

Calculations are detailed in appendix 5.

	2N, 100°C, 4 hours 40 kg/h	2N, 100°C, 8 hours 20 kg/h	6N, 100°C, 8 hours 20 kg/h	12N, 100°C, 8 hours 20 kg/h
Scenario 1 100% UO_2 10 μm	<u>Power : 5.4 kW</u> <u>NOx : 2.2 Nm³/h</u>	Power : 2.7 kW NOx : 1.1 Nm ³ /h	Power : 1.7 kW NOx : 3.3 Nm ³ /h	Power : 1.7 kW NOx : 3.3 Nm ³ /h
Scenario 2 50% UO_2 10 μm 50% U 10 μm	Power : 27.8 kW NOx : 4.9 Nm ³ /h	<u>Power : 13.4 kW</u> <u>NOx : 2.5 Nm³/h</u>	Power : 13.4 kW NOx : 3.5 Nm ³ /h	Power : 11.6 kW NOx : 7.3 Nm ³ /h
Scenario 3 50% UO_2 10 μm 50% U 6mm	Accumulation 99% of the total amount of U sludges (dissolution rate is too low)	Accumulation 99% of the total amount of U sludges (dissolution rate is too low)	Accumulation 77% of the total amount of U sludges (dissolution rate is too low)	Power : 11.6 kW NOx : 7.3 Nm ³ /h

table 9

Results of simulations of continuous dissolution

Nota :

Solutions that are underlined have been finally selected.

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Table 9 shows that it is difficult to dissolve continuously a UO_2/U mixture with "big" U particles such as in the scenario 3. In the scenario 4, U particles are a little bit smaller than in scenario 3 and it is possible to dissolve in a continuous way UO_2 particles and U particles of $\varnothing = 500 \mu\text{m}$ with an acidity greater than 2 N but lower than 8 N. The minimum acidity to dissolve continuously UO_2 ($10 \mu\text{m}$) and U ($500 \mu\text{m}$) is 4.2 N. The continuous dissolution, in 4.2 N nitric acid at 100°C during 8 hours, of the sludges (50 % UO_2 , 50 % U) leads to the following results summed up in table 9 bis:

	4.2N, 100°C , 8 hours 20 kg/h
Scenario 4 50% UO_2 $10 \mu\text{m}$ 50% U $500 \mu\text{m}$	Power : 13.7 kW NOx : 3 Nm^3/h

table 9 bis

Results of simulation for scenario 4 of continuous dissolution

92% of the power produced (13.7 kW) is due to the dissolution reaction of U. According to stoichiometries of both U and UO_2 dissolution reactions, 90 % (volume) of the NOx flowrate are composed of NO and 10 % (volume) of NO_2 .

Nota :

Solutions that are underlined have been finally selected.

9.3. DISCUSSION

Continuous dissolution seems to be a better solution than batch dissolution for scenari 1, 2 and 4. Dissolution is instantaneous, but as sludges feed flowrate is controlled, the generated power and NOx flowrate are kept at reasonable values. The most appropriate operating conditions depend on the scenario.

Regarding power generated by dissolution reactions when sludges contain U (scenarii 2, 3 and 4), it seems more reasonable to consider a continuous dissolution during 8 hours rather than 4 hours when sludges contain U.

Therefore, the best process options seem to be :

- scenario 1 : 2 N, 4 hours,
- scenario 2 : 2 N, 8 hours,
- scenario 4 : 4.2 N, 8 hours.

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It is worth noticing that concerning scenario 4, 4.2 N represents the minimum acidity allowing continuous dissolution in 8 hours. Concerning scenario 3 ("big" U particles), table 9 shows that acidity must be high (~12 N) to allow a continuous dissolution in 8 hours. This acidity seems difficult to manage and it seems more convenient to consider a third process option, which would be a continuous step followed by a batch step in this particular case (see § 10).

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10. SIMULATIONS OF MIXED DISSOLUTION OPERATION : CONTINUOUS DISSOLUTION FOLLOWED BY BATCH PROCESSING

As previous simulations show that dissolution of U sludges of 6 mm diameter was possible neither through batch nor through continuous processing, a "mixed" dissolution is proposed.

An industrial way to dissolve U (6mm) and UO_2 (10 μm) mixed sludges could be to continuously feed the dissolver (2N, 100°C) with sludges in order to continuously dissolve UO_2 sludges 10 μm . U sludges (6mm) accumulate in the dissolver as their dissolution rate is very low in 2N nitric acid. After 8 hours feeding, the dissolver contain about 80 kg U sludges (the dissolved fraction is neglected). Feeding is stopped and acidity in the dissolver is then increased to 6 or 8N, still at 100°C : batch dissolution of U sludges occurs.

10.1. OPERATING CONDITIONS

The dissolution is a continuous operation during 8 hours, followed by a batch operation until dissolution is totally achieved.

During continuous dissolution, temperature is equal to 100°C and normality is set to 2N.

During batch dissolution, temperature is equal to 100°C and normality of nitric acid is increased instantaneously to 6N or 8N.

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10.2. RESULTS

Results of simulations for the scenarii 3 and 4 are presented in table 10.

		Scenario 3		Scenario 4	
Continuous feed during 8 hours	Acidity (N)	2 N		2 N	
	Temperature (°C)	100°C		100 °C	
	Power generated (kW)	1.6		1.6	
	NOx flowrate (Nm ³ /h)	0.6		0.6	
	Dissolution time	8 hours		8 hours	
Batch operation	Acidity (N)	6 N	8 N	2.25 N	6 N
	Temperature (°C)	100°C	100°C	100°C	100°C
	Power generated (kW)	20.5	32.5	20.2	177
	NOx flowrate (Nm ³ /h)	2.5	17.8	2.5	22.1
	Dissolution time	11 hours	6 hours	8 hours 30'	1 hour
	Total dissolution time	19 hours	14 hours	16 hours 30'	9 hours

table 10

Results of mixed dissolution simulations for scenarii 3 and 4

Nota :

Acidity of 2.25 N has been determined so that the batch step of scenario 4 performed at this acidity and at 100°C produces approximately the same generated power than the batch step (6N, 100°C) of scenario 3 (see table 10), which is 20.5 kW.

10.3. DISCUSSION

This mixed dissolution seems to be appropriate to solve the problem of "big" U particles. For scenario 3, the most appropriate conditions seem to perform batch dissolution at 6N : required time is long, but maximum generated power and NOx flowrate are kept at reasonable values. Moreover, managing a 6N solution is more convenient than a 8 N solution.

For scenario 4, continuous dissolution operated at 4.2N (see §9) is a suitable solution. Mixed dissolution at 2.25N also represents a possible way.

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11. CONCLUSION

This study has consisted in modeling the dissolution of sludges containing dioxide uranium and metallic uranium in nitric acid solutions.

An adapted model has been developed using SPEEDUP software on the basis of a qualified model previously developed by SGN.

A study of different kinetics of dissolution of dioxide uranium in nitric acid solutions has been performed in order to choose the most appropriate kinetic law. Dissolution of metallic U has also been studied to select a kinetic law.

Four scenarii have been studied (see §3), corresponding to various particle size distributions and compositions of sludges (UO_2 , U). For each scenario, several operating conditions have been simulated. Simulations have led to the determination of the best operating conditions to take into account the main process requirements (temperature, acidity) : these operating conditions are given in table 11.

	Kind of dissolution operation	Temperature (°C)	Acidity (N)	Dissolution time (hours)	Generated power (kW)	NOx flowrate (Nm^3/h)
Scenario 1 100% UO_2 10 μm	Continuous dissolution	100	2 N	4 hours	5.4	2.2
Scenario 2 50% UO_2 10 μm 50% U 10 μm	Continuous dissolution	100	2 N	8 hours	13.4	2.5
Scenario 3 50% UO_2 10 μm 50% U 6mm	Mixed dissolution (continuous followed by batch dissolution)	100	2 N (continuous) then 6N (batch)	19 hours (8 hours of continuous dissolution, followed by 11 hours of batch dissolution)	20.5 (= maximum power generated during batch dissolution)	2.5 (= max flowrate generated during batch dissolution)
Scenario 4 50% UO_2 10 μm 50% U 500 μm	Continuous dissolution	100	4.2 N	8 hours	13.7	3.0

table 11

Best operating conditions for the four scenarii studied

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On the one hand, small particles (10 μm) dissolve quite easily at 100°C, whatever their composition (UO_2 or U). In order to be able to control reaction, continuous dissolution is the most appropriate process option. Another possibility would be to start operation at low temperature and acidity, and then to increase these two parameters to control dissolution rate. But the uncertainties on reactivity of sludges lead to a difficult control of such an operation.

On the other hand, "big" particles, as U 6 mm in scenario 3, are very difficult to dissolve. Therefore a batch dissolution at higher acidity is the most appropriate process option for these particles.

However, as these "big" U particles are mixed with small UO_2 particles, a simple batch operation would not allow to cope with fast dissolution reaction of small UO_2 particles. Therefore, a mixed dissolution is proposed for the scenario 3 : a first continuous step allows to dissolve small particles, then a batch step allows to cope with "big" U particles.

At an industrial scale, it would be preferable to consider a unique operating procedure to cope with all possible scenarii. This unique operating procedure could be a continuous dissolution (8 hours - 20 kg/h) at 6N and 100°C for all scenarii. Concerning scenario 3, a batch step at 6N must of course be maintained after the continuous step.

Increasing acidity from 2N to 6N may lead to slightly different results from the ones given in table 11. In fact, as acidity increases then the generated power decreases and the NO_x flowrate becomes more important (see the stoichiometries of UO_2 and U dissolution reactions § 4.1 and § 5.1). Furthermore, the major part of generated NO_x is composed of NO_2 as acidity increases (see § 5.1 table 3).

So, for scenarii 1, 2 and 4, the generated power and the NO_x flowrate at 6N differ from the ones at 2N given in table 11 but the order of magnitude remains the same : generated power is a little bit lower and the NO_x flowrate is a bit greater ($\approx 3.5 \text{ Nm}^3/\text{h}$).

Concerning scenario 3, the continuous step at 6N will lead to a higher dissolved fraction of U at the end of this continuous step : therefore, the maximum generated power and the maximum flowrate should be a bit lower than the values given in table 11.

It is worth noticing that actual kinetic characteristics of dissolution of sludges are not well known for the time being. Studied kinetic laws are assumed to be appropriate to simulate dissolution of Hanford sludges, but experiments performed on real sludges would undoubtedly be helpful and even necessary to improve modeling accuracy.

Estimation of NO_x fluxes are used in the design of absorption columns [13].

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APPENDIX 1

DETERMINATION OF PARAMETERS OF SECOND KINETIC LAW OF UO_2 DISSOLUTION

The article referenced [1] deals with batch dissolution of UO_2 powder in nitric acid [1].

Assuming that powder is composed of spherical particles, apparent specific surface area is estimated to 1922 cm^2 on the basis of the particle size distribution detailed in [1].

Kinetic rate is determined from experimental measurements of concentration of dissolved uranium in the dissolver.

Between 60 and 80 minutes, concentration of dissolved U increases linearly and kinetic rate is equal to 1070 mg/min . Kinetic rate per unit of apparent surface area is estimated to $0.556 \text{ mg/min/cm}^2$.

Kinetic law is expressed as :

$$V = k_0 \exp\left(\frac{-E_a}{RT}\right) ([H^+] + [U])^2$$

V	:	dissolution rate ($\text{mg/cm}^2/\text{min}$)
k_0	:	rate constant ($\text{mg/cm}^2/\text{min})/(\text{mol/l})^2$
E_a	:	energy of activation (J/mol)
$[H^+]$	:	molar concentration of nitric acid (mol/l)
$[U]$	:	molar concentration of dissolved uranium (mol/l)
R	:	constant for ideal gases ($R=8.314 \text{ J/mol/K}$)

The value of E_a is assumed to be the same as the one determined for the kinetic law previously used in La Hague plant [4]:

$$E_a = 4.35 \text{ kcal/mol} = 18183 \text{ J/mol}$$

The operating conditions are 95°C and 2.6 N nitric acid. Apparent constant rate k_0 can be determined :

$$k_0 = 14.53 \text{ (mg/cm}^2/\text{min})/(\text{mol/l})^2$$

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APPENDIX 2

DETERMINATION OF THE EXPRESSION OF THE THIRD DISSOLUTION RATE

The rate equation given in literature [2] is :

$$(1) \quad 1 - (1 - X)^{1/3} = k \cdot t$$

X represents the dissolved fraction of UO_2 .

k represents the apparent rate constant (min^{-1}) and t is the time expressed in minutes.

k depends on acidity and temperature as following :

$$(2) \quad k = k_1 [\text{H}^+]^a \exp\left(-\frac{E_a}{RT}\right)$$

with :

- a : degree of dependence on acidity ($a=1.7$)
- k_1 : rate constant ($\text{min}^{-1}(\text{mol/l})^{-a}$)
- E_a : energy of activation (J/mol)
- $[\text{H}^+]$: molar concentration of nitric acid (mol/l)
- T : temperature (K)
- R : constant for ideal gases ($R = 8.314 \text{ J/mol/K}$)

The calculation of the dissolution rate is made assuming that X and k depend only on time. Fraction of dissolved uranium dioxide is expressed as :

$$X = 1 - \frac{m(t)}{m_0}$$

with :

- $m(t)$: mass of uranium dioxide which is not yet dissolved (kg)
- m_0 : initial mass of uranium dioxide (kg)
- X : fraction of dissolved UO_2

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Dissolution rate of uranium dioxide $\left(-\frac{dm}{dt}\right)$ is expressed as a function of the fraction of dissolved uranium :

$$-\frac{dm}{dt} = m_0 \frac{dX}{dt}$$

with :

$$(3) \quad m(t=0) = m_0$$

Derivation of expression (1) with initial conditions (equation (3)) leads to the following system :

$$\begin{aligned} \frac{dX}{(1-X)^{2/3}} &= 3 \cdot k \cdot dt \\ X(t=0) &= 0 \end{aligned}$$

Finally, the expression of the dissolution rate of uranium dioxide is :

$$-\frac{d(m(t))}{dt} = 3 \cdot k \cdot m_0 \cdot \left(\frac{m(t)}{m_0}\right)^{2/3}$$

k depends on acidity and temperature as equation (2) mentioned it.

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APPENDIX 3

DIAGRAM OF THE DISSOLUTION PROCESS MODELED BY PREVIOUS MODEL

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APPENDIX 4

QUALIFICATION OF THE DISSOLUTION MODEL OF LA HAGUE
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APPENDIX 5

CONTINUOUS DISSOLUTION OF SLUDGES

First, dissolution kinetic rate (calculated with the kinetic laws detailed in §4.4.3 and §5.4) is compared to inlet flowrate of sludges. If dissolution kinetic rate is greater than the inlet flowrate of sludges, dissolution is continuous.

Calculations relative to continuous dissolution are performed as following :

- Calculations of inlet mass flowrate of sludges :

Inlet mass flowrate of sludges is calculated such as 160 kg of sludges are fed in the dissolver during dissolution time which is set equal to 4 or 8 hours. Mass flowrate is constant.

- Calculations of power generated by dissolution of sludges :

As acidity is set to a constant value (2, 6 or 12N) for the whole continuous dissolution operation, stoichiometry of the dissolution reaction is known (see §4.1 and §5.1). Then, as specific enthalpy reaction is expressed in function of molar quantity of sludges dissolved, power generated is calculated corresponding to sludges inlet mass flow rate.

- Calculations of NOx flowrate generated by dissolution of sludges :

NOx flowrate is calculated on the basis of the reaction stoichiometry.

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APPENDIX 6

CALCULATION OF THE INITIAL VOLUME OF SLUDGES SOLUTION

Sludges (160 kg on a dry basis) are introduced with water in the dissolver (12% (mass) of dry solids).

The density of the sludges is assumed to be equal to uranium dioxide density (10 500 kg/m³).

Then, it is possible to calculate the initial volume of the sludges solution V_s which is 1188 l.

Nitric acid (12N) is added to get an average acidity of 0.5N.

This volume is calculated :

$$12 V_{\text{HNO}_3} = 0.5 (V_s + V_{\text{HNO}_3})$$

$$V_{\text{HNO}_3} \approx 52 \text{ l}$$

with :

V_{HNO_3} : added nitric acid (12N) volume (l)

V_s : initial volume of the sludges solution (l)

Therefore, total initial volume in the dissolver is equal to 1240 l.

time.

Curves of acidity, temperature, dissolution rate and flowrate of UO_2 dissolved versus(scenario 1) : acidity 2 N, temperature 100°C , one hour heating
First kinetic law of dissolution of UO_2 :

RESULTS OF THE PRELIMINARY SIMULATIONS

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Curves of dissolution rate, flowrate of UO_2 dissolved and amount of UO_2 dissolved versus time.

First kinetic law of dissolution of UO_2 :
(scenario 1) : acidity 2 N, temperature 100°C , one hour heating

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First kinetic law of dissolution of UO_2 :
(scenario 1) : acidity 2 N, temperature 100°C , one hour heating

Curves of temperature and mass flow of nitrous vapors versus time.

Curves of acidity, temperature, dissolution rate and flowrate of UO_2 dissolved versus time.

(scenario 1) : acidity 2 N, temperature 100°C, one hour heating

Second kinetic law of dissolution of UO_2 :

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Second kinetic law of dissolution of UO_2 :
(scenario 1) : acidity 2 N, temperature 100°C, one hour heating
Curves of dissolution rate, flowrate of UO_2 dissolved and amount of UO_2 dissolved
versus time.

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Second kinetic law of dissolution of UO_2 :
 (scenario 1) : acidity 2 N, temperature 100°C , one hour heating

Curves of temperature and mass flow of nitrous vapors versus time.

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Third kinetic law of dissolution of UO_2 :
 (scenario 1) : acidity 2 N, temperature 100°C , one hour heating

Curves of flowrate of UO_2 dissolved and amount of UO_2 dissolved versus time.

BATCH dissolution
Scenario 1 : acidity 0.5 N, temperature 100°C, two hours heating

RESULTS OF THE SIMULATIONS OF BATCH DISSOLUTION

APPENDIX 8

Type Doc.	NT	10510	00	0005	Rév. A
Author	CM	MT	N°	Revisé	Revisé

BATCH dissolution :
Scenario 1 : acidity 0.5 N, temperature 100°C, two hours heating

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Ch. MT					
N° Fiches					
Revision

BATCH dissolution :
Scenario 1 : acidity 1 N, temperature 100°C, one hour heating

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BATCH dissolution :

Scenario 1 : acidity 1 N, temperature 100°C, one hour heating

BATCH dissolution :
Scenario 1 : acidity 1 N, temperature 100°C, two hours heating

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BATCH dissolution :

Scenario 1 : acidity 1 N, temperature 100°C, two hours heating

BATCH dissolution :
Scenario 1 : acidity 2 N, temperature 100°C, one hour heating

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BATCH dissolution :
Scenario 1 : acidity 2 N, temperature 100°C, one hour heating

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BATCH dissolution :

Scenario 1 : acidity 2 N, temperature 100°C, two hours heating

BATCH dissolution :
Scenario 1 : acidity 2 N, temperature 100°C, two hours heating

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BATCH dissolution :

Scenario 2 : acidity 0.5 N, temperature 100°C, two hours heating

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BATCH dissolution :

Scenario 2 : acidity 1 N, temperature 100°C, one hour heating

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BATCH dissolution :
Scenario 2 : acidity 1 N, temperature 100°C, two hours heating

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BATCH dissolution :

Scenario 2 : acidity 1 N, temperature 100°C, two hours heating

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BATCH dissolution :
Scenario 2 : acidity 2 N, temperature 100°C, two hours heating

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BATCH dissolution :

Scenario 2 : acidity 2 N, temperature 100°C, two hours heating

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APPENDIX 9

RESULTS OF THE SIMULATIONS OF MIXED DISSOLUTION

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Scenario 3 : acidity 6 N, temperature 100°C

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Scenario 3 : acidity 8 N, temperature 100°C

Scenario 3 : acidity 8 N, temperature 100°C

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Scenario 4 : acidity 2.25 N, temperature 100°C

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Scenario 4 : acidity 6 N, temperature 100°C

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Scenario 4 : acidity 6 N, temperature 100°C

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