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EFFECTS OF NITRIC ACID ON CRITICALITY SAFETY ANALYSIS

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ABSTRACT

As nitric acid molarity is increased, there are two competing phenomena affecting the reactivity of the system. First, there is interaction between each of the 10 wells in the basket-like insert. As the molarity of the nitric acid solution is increased (it moves from 100% water to 100% HNO_3), the hydrogen atom density decreases by about 80%. However, it remains a relatively efficient moderator. The moderating ratio of nitric acid is about 90% that of water.

As the media between the wells is changed from 100% water to 100% nitric acid, the density of the media increases by 50%. A higher density typically leads to a better reflector. However, when the macroscopic scattering cross sections are considered, nitric acid is a much worse reflector than water. The effectiveness of nitric acid as a reflector is about 40% that of water. Since the media between the wells become a worse reflector and still remains an effective moderator, interaction between the wells increases. This phenomenon will cause reactivity to increase as nitric acid molarity increases.

The second phenomenon is due to the moderating ratio changing in the high concentration fissile-nitric acid solution in the 10 wells. Since the wells contain relatively small volumes of high concentration solutions, a small decrease in moderating power has a large effect on reactivity. This is due to the fact that neutrons are more likely to escape the high concentration fissile solution before causing another fission event. The result of this phenomenon is that as nitric acid molarity increases, reactivity decreases.

Recent studies have shown that the second phenomenon is indeed the dominating force in determining reactivity changes in relation to nitric acid molarity changes. When considering the system as a whole, as nitric acid molarity increases, reactivity decreases.

Key Words: dissolving, nitric acid

1 INTRODUCTION: H-CANYON

H-Canyon is the only operating nuclear chemical separations plant remaining in the United States. It is located at the 310-square-mile Savannah River Site in South Carolina and is owned by the U.S. Department of Energy. H-Canyon employs remote operations for most processes, including dissolving, separations cycles, and waste systems.

In the past, H-Canyon's missions have included recovering U-235, Np-237, and Pu-238 for use in defense, space, and commercial nuclear power purposes. Currently, H-Canyon maintains the capacity to safely and efficiently disposition a large inventory of excess nuclear material from across the Department of Energy (DOE) complex and used nuclear fuel from foreign and domestic research reactors.

H-Canyon processes involve large quantities of fissile solutions, including high enriched uranium and weapons grade plutonium, in geometrically unfavorable tanks. Therefore, criticality safety is of the utmost importance. H-Canyon has an extensive criticality safety program, including criticality safety evaluations for all processes, monthly criticality assessments/walkdowns, and criticality safety training for all personnel with access to the facility.

1.1 The Dissolving Process

Dissolving is the first step in processing material through H-Canyon. For each new type of material to be dissolved, the criticality safety of the operation must be established. A Nuclear Criticality Safety Evaluation must be developed that provides Criticality Safety Limits (CSLs) and controls to ensure all normal and credible abnormal conditions remain subcritical.

There are two dissolvers in use in H-Canyon. One is a 12-foot-diameter, 8-foot-tall, vertical, cylindrical tank. The other is an 8-foot-diameter, 8-foot-tall, vertical, cylindrical tank. The dissolving process utilizes nitric acid as the solvent with various catalysts, if needed. Nitric acid, at the beginning of the dissolving process, is usually in the 4-6 Molar range.

An insert is placed in the dissolver pot to provide some control over geometry during the dissolution process. The insert is a basket-like device with ten long, cylindrical, vertical wells. Each well is 6 inches in diameter, ~18 feet long, and has hundreds of holes to allow for flow of nitric acid in and nitric-acid-fissile solutions out into the bulk solution. To charge the dissolver with nuclear material, a long, thin, vertical metal tube (called a bundle) is pre-loaded with nuclear material and lowered into each well in the insert. The bundles may be constructed of stainless steel if they are to be re-used, or the bundle may be constructed of aluminum if it is to be dissolved along with the nuclear material. A plug may be used to block various wells if the criticality safety evaluation determines that loading all ten wells is not safe for that particular material. Figure 1 shows several views of the 10-well insert.

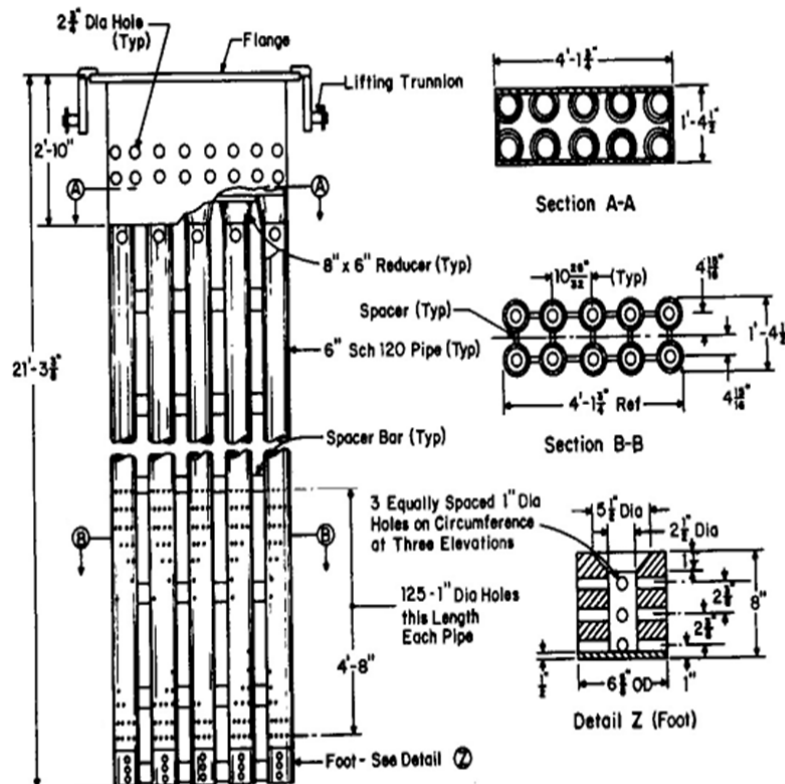


Figure 1 10-Well Insert

2 NITRIC ACID EFFECTS

Nitric acid acts as both a moderator and a reflector. As the percentage of nitric acid is increased (and thereby the molarity is increased), the effectiveness of the media as a moderator and reflector changes. There are several competing effects that nitric acid has on the reactivity of the system.

2.1 Nitric Acid

Nitric acid's chemical formula is ($\text{HNO}_3 + \text{H}_2\text{O}$). Nitric acid molarity (or molar concentration) is calculated by multiplying the density of the solution by the weight percent nitric acid and dividing by the molecular weight. The densities of nitric acid solutions can be obtained from chemical reference books. The molecular weight of HNO_3 is 63.0 moles/gram[1]. For example, 30% nitric acid has a density of 1.18 g/cm³ (1,180 g/L) [2]. Of that 1,180 grams in a liter of solution, 30% of that, or 354 grams is HNO_3 . 354 grams of HNO_3 is equivalent to 5.62 moles (354 g / 63.0 moles/gram = 5.62 moles). Since there are 5.62 moles in a liter of solution, the molarity is 5.62 molar (M). Similarly, the density of 100% nitric acid is 1.50 g/cm³[2], and the molarity is 23.8 M.

A maximum-boiling azeotrope exists for nitric acid at 68%. This is the maximum weight percent at which the boiled vapor maintains the same composition as the liquid. For this reason, 68% nitric acid is the maximum percentage available for use in H-Canyon. However, the acid is routinely diluted with more water so that it is in the 20-30% (4-6 M) range. Although performing modeling studies with up to 100% nitric acid may be somewhat unrealistic, it helps the analyst to better understand the physics involved.

In the dissolver, there are two primary areas of concern. There is the bulk solution, where the fissile material (if present) is well-moderated and at a low concentration. At the beginning of the dissolving process, there is no fissile material in the bulk solution. The other area of concern is the wells, where the material is not well-moderated and is at a high concentration.

2.2 Nitric Acid as a Moderator

The media between the wells plays an important role in increasing or decreasing moderation and interaction between units.

A material's hydrogen content is often the primary measure of its effectiveness as a moderator. The hydrogen atom density is calculated from Eq. 1,

$$N_H = \frac{\rho * 6.022 \text{E}23}{A} * \# \text{ of H atoms per molecule} \quad \text{Eq. 1}$$

where ρ is the density of the material in g/cm³, and A is the molecular weight of the material in g/mole. Atom densities are often multiplied by 1E-24 cm²/barn to obtain an atom density unit of atoms/barn-cm. With a density of 0.9970 g/cm³ and a molecular weight of 18.01 g/mole and two hydrogen atoms per molecule, water has a hydrogen atom density of 0.06665 atoms/barn-cm. With a density of 1.504 g/cm³ and a molecular weight of 63.00 g/mole and only one hydrogen atom per molecule, 100% nitric acid has a hydrogen atom density of 0.01437 atoms/barn-cm. This indicates that 100% nitric acid contains only 21.6% of the hydrogen that water contains, and this implies that nitric acid will be a much worse moderator than water. However, there are other factors that should be considered, including scattering and absorption cross sections.

One parameter used for comparing moderators is the average lethargy gain per collision, ξ . This is given by Eq. 2 [3].

$$\xi = 1 - \frac{(A-1)^2}{2A} \ln \left(\frac{A+1}{A-1} \right) \quad \text{Eq. 2}$$

The ξ value for a compound is more complex. The elemental values of ξ are weighted by the scattering cross sections and summed in order to obtain the average value over the mixture. This is shown in Eq. 3 [4].

$$\bar{\xi} = \frac{\sum_{i=1}^n \sigma_{si} \xi_i}{\sum_{i=1}^n \sigma_{si}} \quad \text{Eq. 3}$$

Table I shows the molecular weight, number density, microscopic scattering and absorption cross sections, and ξ for several compounds and their constituent elements.

Table I Number Densities, Cross Sections, and ξ

Moderator	A (g/mole)	N (atoms/barn-cm)	σ_s (barns) ¹ [5]	σ_a (barns) ¹ [5]	ξ
H₂O	63.00	0.03333			0.9256
H	1.008	0.06665	20.47	0.332	1.000
O	15.99	0.03333	3.78	0.00019	0.1200
HNO₃	18.01	0.01437			0.5546
H	1.008	0.01437	20.47	0.332	1.000
N	14.01	0.01437	10.01	0.075	0.1362
O	15.99	0.04312	3.78	0.00019	0.1200

Higher values of ξ are preferred in order to have a more effective moderator. However, the moderating power of a material also accounts for the macroscopic scattering cross section. The moderating power is shown below in Eq. 4.

$$\text{Moderating power} = \xi \Sigma_s \quad \text{Eq. 4}$$

Also, if a material has a large macroscopic *absorption* cross section, it will not make for a good moderator. Slower neutrons are not useful for fission if they are being absorbed by the moderating material. Hence, the moderating ratio is used to compare moderators as a whole. The moderating ratio takes into account the energy transferred during a collision, the probability of a scattering collision, and the probability of an absorption. The moderating ratio is shown in Eq. 5.

$$\text{Moderating ratio} = \frac{\xi \Sigma_s}{\Sigma_a} \quad \text{Eq. 5}$$

Table II shows the macroscopic scattering and absorption cross sections, the moderating power, and the moderating ratio for water and nitric acid.

Table II Moderating Power & Moderating Ratio

Moderator	ξ	Σ_s (barns)	Σ_a (barns)	Moderating power	Moderating ratio
H₂O	0.9256	1.490	0.02214	1.380	62.32
HNO₃	0.5546	0.6011	0.005858	0.3334	56.91

¹ These are fission-spectrum averaged cross sections.

Comparing the moderating ratios of water and nitric acid shows that water is a better moderator than nitric acid, but not by much. Nitric acid is still a very effective moderator. This is due to the fact that although hydrogen has a higher scattering cross section than nitrogen or oxygen, it also has a much higher absorption cross section.

2.3 Nitric Acid as a Reflector

Nitric acid may not be an obvious choice for a reflecting material, but it does have some reflective properties. If one just considers the density of the solution, it appears nitric acid may be a very effective reflector. As nitric acid molarity is increased, the density of the solution also increases. If the nitric acid molarity were zero, then the solution would be 100% water, and the density would be 0.9970 g/cm^3 . However, if the solution were theoretically 100% HNO_3 , the molarity would be 23.8 M, and the density would be 1.504 g/cm^3 . For a hydrogenous material with 50% greater density than water, nitric acid has the potential to be a good reflector.

However, it is also important to look at the elastic scattering cross sections of the materials. The macroscopic elastic scattering cross sections for several compounds and their constituent elements are given in Table III.

Table III Macroscopic Scattering Cross Sections

Moderator	Σ_s (barns)
H₂O	1.490
H	1.364
O	0.1260
HNO₃	0.6011
H	0.2942
N	0.1439
O	0.1630

The macroscopic scattering cross section takes into account the increased density of HNO_3 and is only 40% that of water. This is because the hydrogen atom density of 100% nitric acid is much lower than the hydrogen atom density of water (see Table I), and the scattering cross sections of nitrogen and oxygen are not high enough to make up for the decrease in hydrogen. This indicates that nitric acid is only 40% as effective as a reflector than water even though it is 50% denser. Therefore, nitric acid is a poor reflector, especially compared to water.

3 RESULTS

In the two regions of concern (inside the wells and the bulk solution), each property of the material (as a reflector and as a moderator) has a varying effect. SCALE 5.0/KENO VI [6] was used to model the dissolver with varying acid molarity in the wells and bulk solution.

3.1 Bulk Solution

In the bulk solution, the media acts as both a reflector and a moderator. It is a reflector because it surrounds the wells that contain the high concentration fissile solution. It also acts a moderator because there are multiple wells and interaction between them.

As discussed in Section 2, increasing the molarity of nitric acid causes it to become a much worse reflector. However, it still remains a very effective moderator (nearly as effective as water). This leads to more interaction between the wells, and k_{eff} increases significantly as the molarity in the bulk solution approaches 23.8 M (100% HNO_3), as shown in Figure 2.

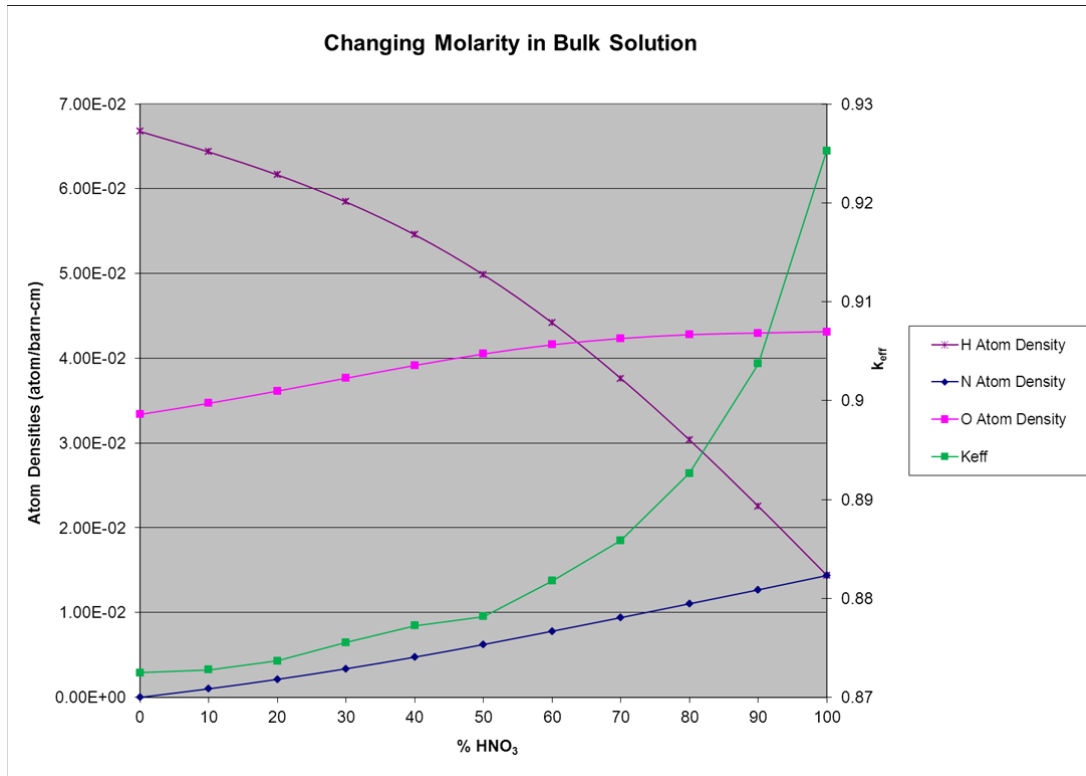


Figure 2 Change in Atom Densities and k_{eff} as Bulk Molarity Changes

3.2 High Concentration Solution in the Wells

In the high concentration solution in the wells, the media only acts as a moderator. Although nitric acid does remain an effective moderator, it is a worse moderator than water. Therefore, as the molarity inside the wells is increased and approaches 23.8 M (100% HNO_3), k_{eff} decreases slightly. This decrease is due to the neutrons having fewer hydrogen atoms with which to collide and slow down before reaching the energy threshold for fission. Therefore, the neutrons are more likely to escape the high concentration solution before causing another fission event.

3.3 Overall

It is interesting to vary the molarity of the bulk solution and solution in the wells independent of each other to determine the competing effects. However, in reality, the molarity will be the same throughout the dissolver vessel, both in the wells and in the bulk solution. Therefore, it is important to vary the molarity in both places at the same time. When this is done, as the molarity increases, k_{eff} decreases slightly. This indicates that the molarity in the wells is the dominating effect, and assuming zero molarity is conservative.

This makes sense because that is where the fissile material is located and the effects there will have a larger impact than where there is no fissile material in the bulk solution.

4 CONCLUSIONS

It is important for criticality safety analysts to understand the physics occurring in the different regions of their systems being analyzed. If a study had not been performed where the molarity in each region was changed independently of each other, all the effects of nitric acid would not have been discovered and understood. Since changing the molarity in the wells is the dominating effect, it would be thought that it was the only effect, and the physics would not be investigated. The problem then would be, if the insert design was changed to have the wells closer together, the change in molarity in the bulk solution may then unknowingly become the dominating effect. If the analysts had continued with the assumption that zero molarity was conservative, it could adversely affect the criticality safety of the operations. This is why understanding the underlying physics of criticality safety is paramount to high-quality criticality safety analyses.

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