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Secondary Cleanup of Idaho Chemical Processing Plant Solvent

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ABSTRACT

Solvent from the Idaho Chemical Processing Plant (ICPP) (operated by Westinghouse Idaho Nuclear Company, Inc.) has been tested to determine the ability of activated alumina to remove secondary degradation products — those degradation products which are not removed by scrubbing with sodium carbonate.

INTRODUCTION

All existing reactor fuel reprocessing plants use the Purex solvent extraction process for recovery of the fissionable materials from spent fuel elements. The head-end of the Purex process involves dissolution of the oxide fuel in nitric acid to yield a solution containing ~200 g of heavy metals per liter, in 3 to 4 $\underline{M}$ HNO_3. This solution is then contacted with a 10 to 30 vol % solution of tri-n-butylphosphate (TBP) in a normal paraffinic hydrocarbon (NPH) diluent. The uranium and plutonium are preferentially extracted into the organic phase, leaving the bulk of the fission products in the aqueous raffinate. The extract is then scrubbed with nitric acid to increase the separation from fission products, and the heavy metals are stripped from the solvent.

The TBP-NPH used in these processes is degraded by radiation damage and by hydrolytic and dealkylation reactions with the nitric acid. A variety of methods have been proposed to minimize the cleanup problems encountered when the degradation products accumulate in the used Purex process solvent. In an earlier study, we found that scrubbing with sodium carbonate solutions (the current practice in Purex plants) was the preferred primary solvent cleanup treatment, unless sodium in the effluent must be restricted (1).

The secondary degradation products (i.e., those remaining after the primary cleanup) can cause problems with phase separation and retention of cations. Since the identities and chemical properties of the important contaminants are unknown, secondary cleanup studies must be conducted using actual recycle solvent. We have previously studied secondary cleanup of Savannah River Plant (SRP) solvent (2) and report here our latest studies, which involved secondary cleanup of Idaho Chemical Processing Plant solvent.

EXPERIMENTAL METHOD

The solvent (~10% TBP-NPH) received from ICPP was first treated with 0.2 volume of 0.2 M Na_2CO_3 [to remove any dibutyl phosphate (DBP) or monobutyl phosphate (MBP) formed during storage], filtered through #40 Whatman paper filters, acidified by contact with 0.04 M HNO_3, and dried by passage of one volume of dry air per min at 60°C for several hours. The solvent was then passed, at a rate of either 1 mL/min (3.5 mL/cm^2•min) or 2 mL/min (7.1 mL/cm^2•min), through a small bed containing activated alumina (Alcoa F-1, 60-120 mesh). The initial plans were to use ~1.3 g of activated alumina in a bed, as was used in earlier studies of SRP solvent (2). However, the small degree of degradation of the ICPP solvent led to large treatable solvent volumes, and the bed size was decreased to 0.5 g to allow determination of approximate bed capacities for the available solvent. The alumina bed (~0.6 cm^3, with a length-to-diameter ratio of 3.3) was contained in an 8-mm-OD, 6-mm-ID glass tube with a jack-leg (See Fig. 1) and was immersed in a beaker of water heated to ~45°C for temperature control.

The solvent leaving the treatment bed was collected in 10- or 20-mL samples and subjected to quality checks. The primary measurements to determine column effectiveness were of the interfacial tension against, and the phase-separation time of the solvent from, 0.2 M Na_2CO_3. The ruthenium content of the solvent was not sufficient to allow determination of ruthenium removal by the column. Anionic surfactant concentrations were too low to be determined by the methylene blue method (3). The concentrations of acidic impurities were too small to be determined by the conductivity method, and plutonium retention gave ambiguous results.

Standard Quality Tests

The following quality tests were done on the effluent solvent from the column tests.

Phase-separation time. The phase-separation time was determined by placing 2 mL of the organic solvent and 2 mL of 0.2 M Na_2CO_3 in a glass vial of ~1.2-cm diam and mixing by slow inversion several times. The separation time was taken to be the time for the emulsion to collapse to one layer of drops at the interface. All these determinations were done by one individual for maximum consistency in results. Even so, this must be considered an inexact method. It is a necessary measurement, however, since phase separation from sodium carbonate solutions is a problem area with degraded solvent.

Interfacial tension. The organic solvent sample to be tested was first equilibrated with the sodium carbonate solution. A small quantity of the separated aqueous phase was drawn into a 0.2-mL micrometer

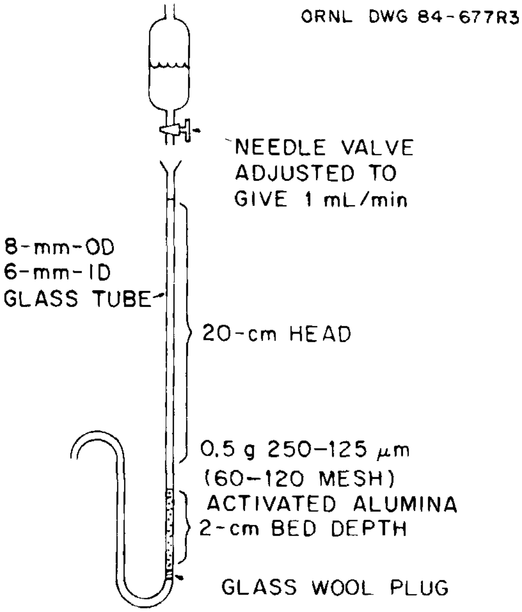

Fig. 1. Typical column for secondary cleanup tests for ICPP solvent

syringe (Gilmont Instruments, Inc., Great Neck, NY) equipped with a 0.0635-cm-OD flat-ended, stainless steel needle. The syringe was then mounted with the needle tip below the surface of the equilibrated organic phase. Drops of aqueous solvent were slowly dispensed, and the volume reading of the micrometer dial was recorded as each drop fell. The interfacial tension was calculated for each drop (Attachment A) and the average determined for several drops (4).

Plutonium retention. The organic samples were contacted with a plutonium standard that contained 37.5 g Pu/L in ~2 M HNO_3. The organic phase was shaken for 10 min three times with equal volumes of water and allowed to stand overnight after the last contact. The plutonium retention is the gross alpha count on the final organic phase.

PROCEDURES AND RESULTS

SRP Solvent Studies

The previously studied SRP solvent was treated with base as the last solvent cleanup step, as contrasted with this study's ICPP procedure, which uses a final scrub with dilute acid. It was suspected that the acid or base might react with materials removed by activated alumina and could affect performance results for the sorbent bed. As a preliminary test, we acidified SRP solvent, dried it by passage of dry air at 60°C, and treated it by passage through 1.3 g of activated alumina at a rate of 1 mL/min. The degree of improvement in solvent quality and the column volumes of solvent treatable by this method were essentially identical to our results when the solvent was treated with base. This demonstrates that the chemical form of the secondary degradation products that are removed by treatment with activated alumina either is unaffected by base or acid treatment or that, in each case, any differing forms are equally well removed.

Determination of Acidic Impurities

German workers recently reported(5) that the levels of acidic impurities could be determined by converting these impurities to their sodium salts and determining the conductivity of the solvent after diluting 50% with absolute alcohol. They determined that various types of impurities can be classified by contacting the solvent with scrub solutions of various basicity. The long-chain acids are converted to their sodium salts by treatment with 0.5 M $NaHCO_3$; the long-chain organophosphoric acids are converted to their sodium salts by

Table 1. Specific conductance of acidic impurities in ICPP solvent tests

Test solution concentration (M)	Conductance of model acidic impurities[a] Lauric acid (mho)	Butyl lauryl phosphate (mho)	2,4-Pentanedione (mho)
0	1.22×10^{-6}		
0	1.16×10^{-6}		
10^{-5}	1.39×10^{-6}	1.43×10^{-6}	1.33×10^{-6}
10^{-5}		1.35×10^{-5}	1.43×10^{-6}
10^{-4}	1.39×10^{-6}	1.56×10^{-6}	1.47×10^{-6}
10^{-4}			1.53×10^{-6}
5×10^{-4}	1.92×10^{-6}	1.82×10^{-6}	1.75×10^{-6}
5×10^{-4}	2.22×10^{-6}		
1×10^{-3}	3.45×10^{-6}	4.0×10^{-6}	3.03×10^{-6}
1×10^{-3}		3.57×10^{-6}	3.1×10^{-6}

[a] Conductance of standard TBP diluted 50% with ethanol was 9.43×10^{-7} mho. Conductance of absolute ethanol used in making test solutions was 7.4×10^{-7} mho.

treatment with 0.25 M Na_2CO_3; and the β-diketones are converted to sodium enolates by treatment with 0.5 M NaOH. We have confirmed this report by measuring the conductivity of solutions of the sodium salts formed from lauric acid, butyllauryl phosphate, and 2,4-pentanedione in 30% TBP-NPH diluted 50% with absolute alcohol. It was found necessary to use the 50-50 dilution to make up standard solutions that remain stable in the concentration range of 10^{-3} to 10^{-5} M. The sodium salt of lauric acid was available commercially, and this was dissolved directly in the 50-50 solvent/alcohol solution to obtain a 10^{-3} M standard; the other concentrations of lauric acid tested were made by dilution of this standard. The butyllauryl phosphate and the 2, 4-pentanedione were dissolved in 30% TBP-NPH, scrubbed with 0.1 volume of 50% NaOH to form the sodium salts, and immediately diluted with ethanol. The conductivities were determined using a YSI Model 31 conductivity bridge. Results are given in Table 1.

The data indicate similar conductivities of the sodium salts of any of the model compounds. Therefore, all the data were fitted to yield the linear least squares equation:

$$C = (1.2559 \pm 0.086) \times 10^{-6} + [(2.042 \pm 0.16) \times 10^{-3}][\underline{M}] \; , \qquad (1)$$

where C is the specific conductivity and [M] is the molar concentration of the sodium salt of the impurity. The standard error of the regression fit is 2.82×10^{-7}, which indicates an ability to determine concentrations within about ± 10^{-4} M. The low degree of degradation of the ICPP solvent gave conductances lower than the uncertainty of the method, but the method might be useful for solvent with higher levels of degradation products.

Cleanup of ICPP Solvent at 45°C

Dried ICPP solvent was passed through 0.504 g of dry activated alumina at a flow rate of 1 mL/min. Data on the phase-separation times and interfacial tensions of effluent samples are shown in Fig. 2. The interfacial tension and phase-separation time for untreated solvent vs 0.2 M Na_2CO_3 were 7.2 dyn/cm and 30 to 35 s, respectively. The interfacial tension was greatly increased (to ~23 dyn/cm), and the phase-separation time was decreased to ~15 to 20 s by passage through the activated alumina bed. The lowest phase-separation time observed by our method was ~15 s. The interfacial tension began to decrease and the phase-separation time to increase after ~800 mL (1300 column-volumes) of solvent had been treated. It appeared that the column had been completely loaded by ~1200 mL (1960 column-volumes) of the solvent. After ~1350 mL of solvent had been treated, the test was stopped overnight and restarted the next day. The quality of the subsequently treated solvent was then seen to improve, a phenomenon also noted in other tests and discussed later. This may be the result of a slow reaction between the adsorbed material and the alumina bed, or it may result from channeling in the small adsorption bed. This peculiar behavior makes it difficult to define the column capacity. In these studies, the column capacity will be defined as the volume treated at the middle of the first increase in the phase-separation time (~1100 mL or 1800 column-volumes), realizing that solvent passing through the column after that time was sig-

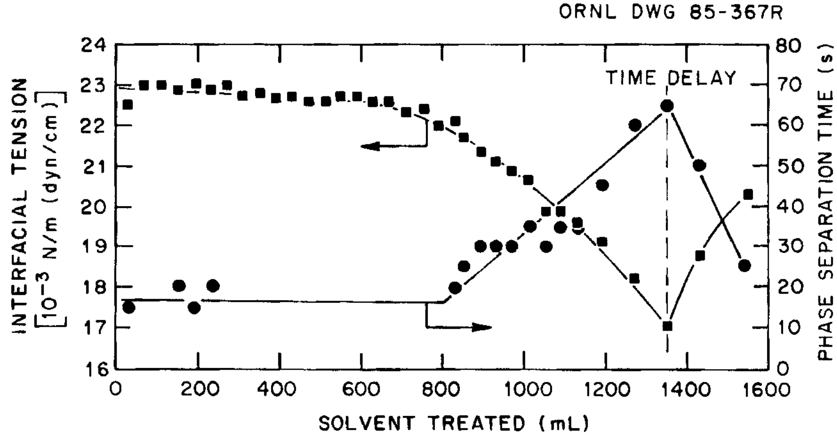

Fig. 2. Results for ICPP solvent treated by passage through 0.504 g of activated alumina at 45°C with a flow rate of 1 ml/min.

nificantly improved in quality. The shape of the curve after the minimum interfacial tension indicates that the actual capacity of the column is probably nearer to 1500 mL (2400 column-volumes). Additional loading of the columns was not attempted because of the limited volumes of ICPP solvent available.

The phase-separation time of treated solvent was observed to exceed that of untreated solvent near the end of this and other tests. This is a phenomenon called "rollover" which can occur during adsorption of multiple impurities from a stream (6).

Figure 3 shows the correlation of interfacial tension with the phase-separation time (both vs 0.2 $\underline{M}$ Na_2CO_3) for the effluent (treated) solvent. The phase-separation time can be predicted from the interfacial tension by the following least-squares-determined linear equation:

$$PST = (-7.95)(IT) + 197, \tag{2}$$

where IT is the interfacial tension (in dyn/cm) and PST is the phase-separation time in seconds. Thus, either of these measurements can be used to define the quality of treated solvent by this method. The interfacial tension data are probably more precise than those for phase-separation time, but it takes slightly longer to make the tension measurements. Note, however, that the characteristics of the untreated solvent do not agree with the correlation of Eq. (2) for treated ICPP solvent.

Steam-Stripping

The column containing the activated alumina sorbent bed was drained and steam-stripped after treatment of the ICPP solvent. For

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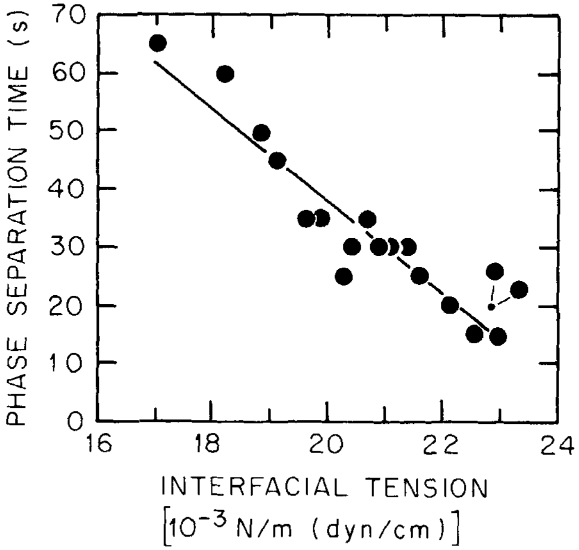

Fig. 3. Correlation of phase separation time with interfacial tension.

this procedure, the column tip was inserted into one hole of a two-hole rubber stopper for a boiling flask. A tube inserted into the other hole of the stopper was attached to a rubber hose that was then submerged in water; this acted as a vent to prevent pressure buildup and expulsion of the packed bed from the column. The steam passing through the column partially condensed in the packed bed, then percolated to the top, where it was removed by suction. Thus, the steam-stripping was accompanied by some upward flushing of the bed with hot water. This flushing was observed to remove much of the oily material from the activated alumina. Nearly 2.5 mL of condensate was collected from the top of the bed during the 2.5-h steam treatment. The bed was subsequently dried at 90°C and was then easily removed from the column. The color of the bed changed from deep brownish-yellow to pale tan early in the steam treatment process.

Reloading of Steam-Stripped Column

The steam-stripped column and sorbent bed were then dried at 325°C and used to treat additional solvent. Results of the experiments (Fig. 4) indicate a column capacity of ~600 mL (980 column-volumes), which is about half of the capacity of the fresh activated alumina. This result, with the crude regeneration method used, makes it likely that a more efficient steam-stripping and/or hot-water-wash method could give nearly complete regeneration.

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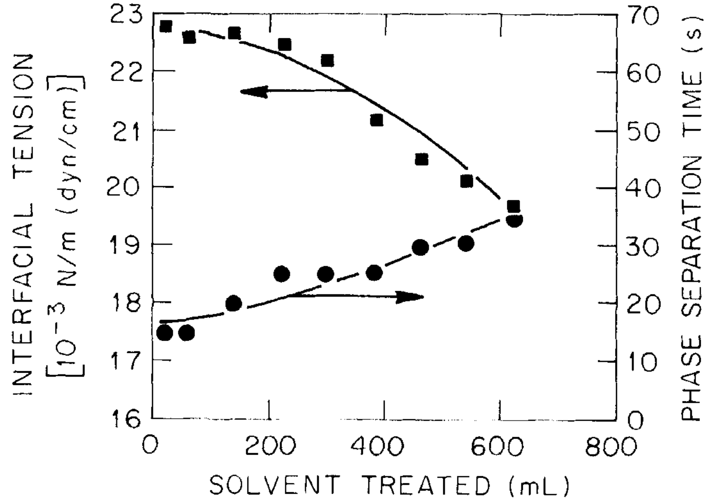

Fig. 4. Results for ICPP solvent treated by passage through regenerated alumina bed at 45°C with a flow rate of 1 ml/min.

Effect of Bed Residence Time

Dried ICPP solvent was passed through 0.500 g of dry activated alumina at a flow rate of 2 mL/min (twice the previous flow rate) to examine the influence of bed residence time on the effectiveness of solvent cleanup. The improvements in interfacial tension and phase-separation time were significantly poorer than improvements obtained with the 1 mL/min flow rate (Fig. 5). The volume of solvent processed before the first increase in phase-separation time was approximately the same as with the lower flow rate. However, our column was small, with a short residence time, and any column used in a process operation would likely have a solvent residence time significantly longer than any we have examined.

Effect of Increasing TBP Content

For a single test, the TBP content of the solvent was increased to 30 vol %, followed by drying of the solvent. The quantity of solvent available at that time was too small to allow the use of even the 0.5-g beds used in the other tests. For this test only, the bed weight was decreased to 0.25 g, and the flow rate was decreased to 0.5 mL/min to maintain the same bed residence time. The untreated solvent fed to the column had a phase-separation time and interfacial tension vs 0.2 $\underline{M}$ Na_2CO_3 of 25 s and 8.1 dyn/cm, respectively. The results of the test are shown in Fig. 6. The increase in phase-

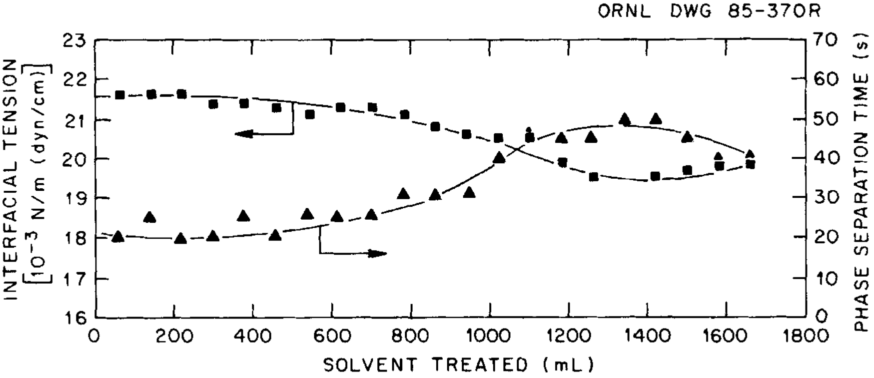

Fig. 5. Results for ICPP solvent passed through 0.500 g activated alumina bed at 45°C with a flow rate of 2 mL/min.

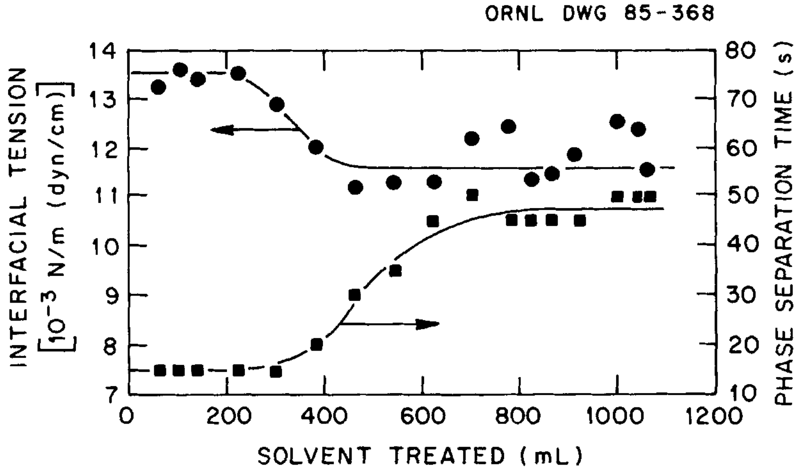

Fig. 6. Results for ICPP solvent with TBP increased to 30 vol%, passed through 0.5 g activated alumina bed at 45°C with a flow rate of 0.5 mL/min.

separation time occurred at ~470 mL (1550 column-volumes), in good agreement with the 1100 mL (1800 column-volumes) found with the lower TBP content. Thus, it appears that the TBP content does not have a significant effect on the volume of solvent that can be treated with activated alumina.

Plutonium Retention

The plutonium retention tests gave unreproducible results, probably due to the formation of plutonium polymer. Earlier studies, using SRP solvent, indicated 90% of the materials that complex plutonium were removed by passage through the activated alumina column, and the fraction removed did not decline significantly during the time preceding the break in phase-separation time.

CONCLUSIONS

The interfacial tension and phase-separation time of ICPP solvent vs sodium carbonate solutions can be greatly improved by passing dried solvent through a bed of activated alumina. The number of bed volumes of solvent that can be treated with a given column was much greater than the number for SRP solvent given similar treatment (2). This results from the decreased degradation of the ICPP solvent. Steam-stripping can be used to remove most of the organic materials from the used sorption bed, resulting in a free-flowing bed that can be easily handled and that has at least 50% of the original bed capacity regenerated. The conductivity method for determining the concentration of acidic impurities in reactor fuel reprocessing plant solvent (5) could not be used with the ICPP solvent, because of the low levels of impurities present.

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ATTACHMENT A. BASIC PROGRAM FOR CALCULATING INTERFACIAL TENSIONS FROM DROP SIZES

```
 10 CLS:IF IT<>0 THEN PRINT "IT = ";IT
 20 PRINT:PRINT:V=0:N=0
 30 INPUT "WHAT IS THE SYSTEM TESTED";I$
 40 LPRINT I$:LPRINT:PRINT
 50 INPUT "WHAT IS DROP VOLUME (HIT ENTER IF THERE ARE NO FURTHER DROPS)
    ";VN
 60 LPRINT VN
 70 IF VN=0 THEN 100
 80 N-N+1:V=V+VN
 90 GOTO 50
100 INPUT "WHAT IS THE DENSITY OF THE ORGANIC PHASE (HIT ENTER IF NO
    CHANGE)";DO
102 IF DO = 0 THEN DO = D1
104 D1 = DO
110 V1=V/N/(.0635) 3
120 IF V1<=1.5 GOTO 160
130 V1=LOG(V1)
140 F=.2754-.0157*V1-.0002357*V1^2
150 GOTO 180
160 V1=LOG(V1)
170 F-.26056+.021385*V1-.02267*V1^2
180 INPUT "WHAT IS THE AQUEOUS DENSITY (HIT ENTER IF NO CHANGE)";DA
182 IF DA = 0 THEN DA = D2
184 D2 = DA
190 IT=V/N*(DA-DO)*980.7*F/.0635
200 PRINT "IT= ";IT
210 LPRINT "THE AQ DENSITY IS ";DA; ".  THE ORIG DENSITY IS ";DO;"."
220 LPRINT:LPRINT "THE INTERFACIAL TENSION IS ";IT
230 LPRINT "--------------------------------------------":LPRINT:LPRINT
240 GOTO 10
250 END
```

This program solves the following equations:

$$\gamma = VFg(d_2 - d_1)/r$$

where:

γ = interfacial tension, 10^{-3} N/m (dyn/cm),
V = drop volume, cm^3,
d_2 = density of heavy phase, g/cm^3,
d_1 = density of light phase, g/cm^3,
g = acceleration due to gravity = 980.7 cm/s^2,
r = radius of needle tip, 0.0635 cm in this case, and
F = correction factor where:
$F = 0.26056 + 0.021385[\ln(V)] - 0.02267[\ln(V)]^2$, for $(V/r^3 < 1.5)$;
$F = 0.2754 - 0.0157[\ln(V)] - 0.0002357[\ln(V)]^2$, for $(V/r^3 > 1.5)$.