CONF-9106203--6

WHC-SA-1170-FP

Silver-Catalyzed PuO_2 Dissolution with Persulfate

Prepared for the U.S. Department of Energy
Assistant Secretary for Defense Programs

Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

WHC-SA--1170

DE91 018153

Silver-Catalyzed PuO_2 Dissolution with Persulfate

F. D. Fisher
G. S. Barney
T. D. Cooper
M. J. Duchsherer

Date Published
June 1991

To Be Presented at
15th Annual Actinide
Separations Conference
Charleston, South Carolina
June 17-20, 1991

Prepared for the U.S. Department of Energy
Assistant Secretary for Defense Programs

Westinghouse Hanford Company
P.O. Box 1970
Richland, Washington 99352

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

NARRATIVE

SLIDE 1

Persulfate ion, or more exactly the peroxydisulfate ion, in the presence of the silver ion effects the rapid dissolution of high-fired (fired at 1,000 °C) plutonium-dioxide at room temperature. The effect in slightly warmed solutions is similar. Dissolution is effected in two steps (1) the oxidation of the Ag^{+} to Ag^{+2} by the persulfate ion, and (2) the oxidation of the PuO_2 by the Ag^{+2}, to yield an overall reaction in which the Pu(IV) ion is oxidized to a Pu(VI), plutonyl ion and the persulfate ion is reduced to yield two sulfate ions.

The solution changes to a dark brown-black color representative of the Ag^{+2}, then takes on an orange-brown color representative of the plutonyl (VI) ion.

SLIDE 2

A rose-colored plutonyl (V) ion product may result in the presence of a somewhat reducing substrate agent. All these colors, however, are masked by the very intense dark brown-black argentic color until the AG^{+2} and persulfate ions are exhausted through reaction with plutonium dioxide or through side reactions with water as shown. The oxidation of water becomes very rapid at elevated temperatures. Standard conversion processes require that the Pu(VI) be reduced to either a Pu(III) or Pu(IV) valence. This reduction can be easily completed by standard methods such as the addition of hydrogen peroxide or ferrous sulfate, or electrolytically.

SLIDE 3

The next few slides examine the influence of dissolution variables on the dissolution of high-fired PuO_2 (fired at 1,000 °C). Differences in dissolution rates for two persulfate concentrations are shown in this slide. In solutions with an excess of PuO_2, there appears to be a positive correlation between persulfate concentration and the dissolution rate.

SLIDE 4

Differences in dissolution rates are shown for three silver concentrations on this slide. In solutions with an excess of PuO_2 there appears to be a positive correlation between silver concentration and the dissolution rate.

SLIDE 5

Differences in dissolution rates are shown for five nitric acid concentrations on this slide. In solutions with an excess of PuO_2, the optimum nitric acid concentration appears to be somewhere between 3 and 4 M.

SLIDE 6

Differences in dissolution rates for four different temperatures are shown on this slide. At temperatures in excess of 40 °C, the persulfate ion and the silver ion are rapidly depleted by side reactions and the reaction stops prematurely.

SLIDE 7

Differences in dissolution rates for two different dissolvent-to-PuO_2 ratios are shown on this slide. It appears that the rate of dissolution essentially is independent of the amount of PuO_2 present for examined regime.

SLIDE 8

Dissolution-rate stoichiometry is examined on this slide. There is an increasing loss of persulfate ion to oxidation of water with increasing temperature.

SLIDE 9

Overall optimum conditions are shown on this slide. The optimum conditions include dilute concentrations of persulfate and silver in a 3 M nitric acid solution. Note that due to the moderately exothermic nature of the reaction sequence, the reaction will often autocatalytically heat from room temperature to the optimum of 40 °C.

SLIDE 10

Differences in dissolution rate are compared for chemically catalyzed silver dissolution, electrochemically catalyzed dissolution (catalyzed electrochemical plutonium-oxide dissolution [CEPOD]), and traditional dissolution in a concentrated nitric acid/dilute hydrofluoric acid bath. As expected, the catalyzed solutions dissolve the PuO_2 more rapidly than the uncatalyzed dissolution.

SLIDES 11 AND 12

Differences in the effect of the sulfate ion on the distribution coefficient for the extraction of plutonium in tributyl phosphate (TBP) solutions are shown in the next two slides. Increases in sulfate concentration appear to inversely affect the ability of TBP to extract plutonium from nitrated solutions; the presence of aluminum supplied by aluminum nitrate nonahydrate significantly reduces the deleterious effect of the sulfate ion.

Rich dissolver-product solutions are stable as plutonyl sulfate is quite soluble. Plutonium (IV) sulfate, however, is only sparingly soluble and the potassium plutonium sulfates are quite insoluble. Dissolver solutions containing more than 6 to 10 g/L should be made 1-M aluminum before valence adjustment. Such solutions when made 7 to 8 M in total nitrate ion with additional nitric acid are stable; plutonium values are rapidly and totally extracted onto the strong-base anion-exchange resin, Lewatit* MP-500FK (extraction onto similar resins produced by other manufacturers would be expected).

*Lewatit is a trademark of Bayer Chemical - Germany.

SLIDE 13

The results of experimental extractions from various heavily contaminated substrates is shown on this slide. A variety of material types has been tested for plutonium dissolution using the silver-persulfate technology with impressive degrees of success. Additional testing is planned for FY 1992.

SLIDE 14

Removal of plutonium values from other scrap and waste materials is desirable and effective with the silver-persulfate system as dissolution procedure and equipment are simple; a stirred pot is all that is required along with some means of subsequently separating product solutions from barren solid residues. The dissolution proceeds rapidly in cold or only warmed solutions, no extremely corrosive reagents are used, and process equipment or non-plutonium substrates are not severely attacked.

DISTRIBUTION

Number of copies

ONSITE

34 Westinghouse Hanford Company

G. S. Barney	T5-12
Information Release Administration	R1-08
Document Processing and Distribution	L8-15

Silver–Catalyzed PuO_2 Dissolution with Persulfate

G. S. Barney

T. D. Cooper

M. J. Duchsherer

F. D. Fisher

Dissolution Reactions

1. Overall dissolution reaction

$$PuO_2 + S_2O_8^{2-} = PuO_2^{2+} + 2SO_4^{2-}$$

2. Catalytic reactions

$$2Ag^{+} + S_2O_8^{2-} = 2Ag^{2+} + 2SO_4^{2-}$$

$$2Ag^{2+} + PuO_2 = 2Ag^{+} + PuO_2^{2+}$$

29106014.2

Side Reactions

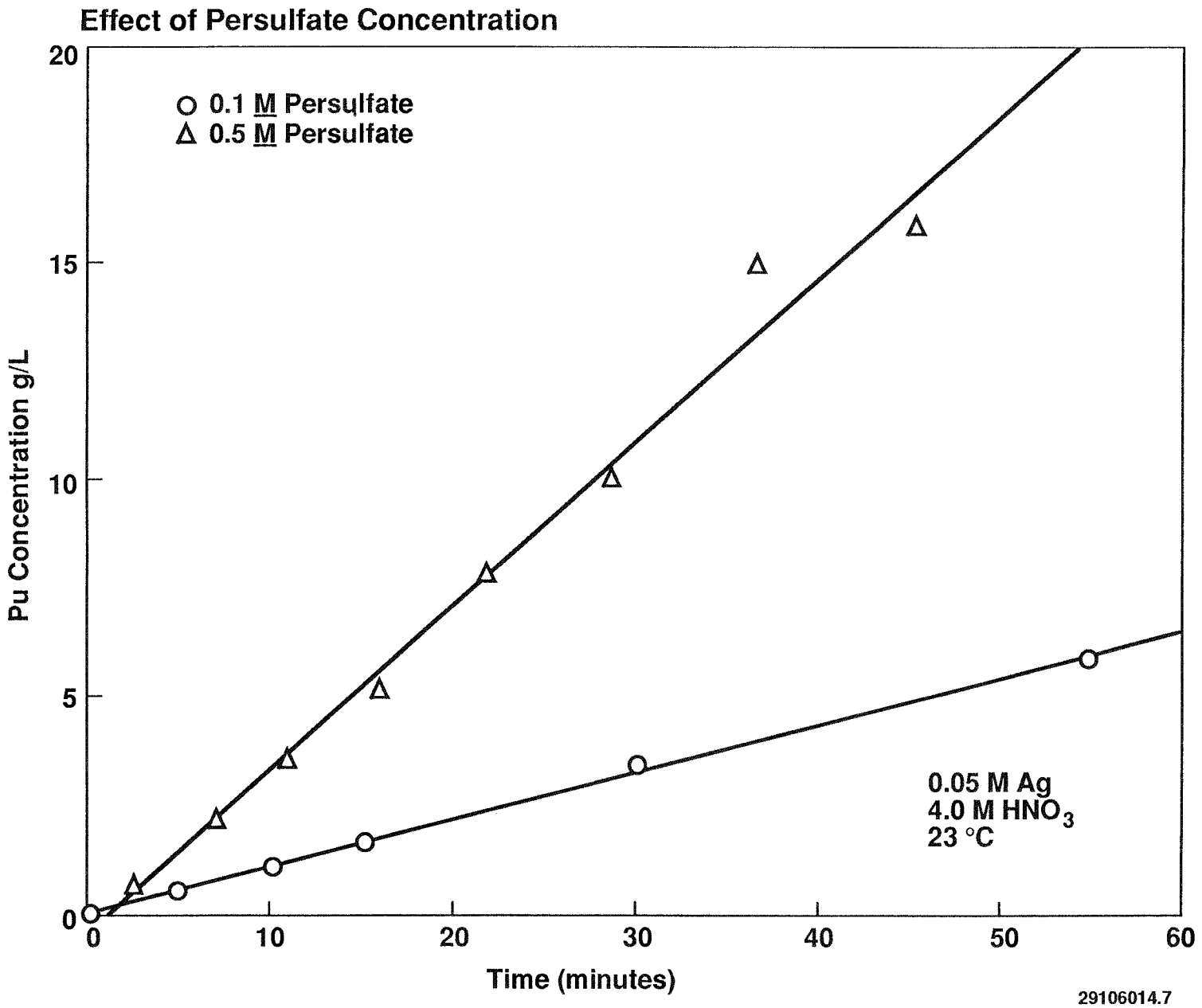
1. Ag(II) oxidation of water

$$4Ag^{2+} + 2H_2O = 4Ag^{+} + O_2 + 4H^{+}$$

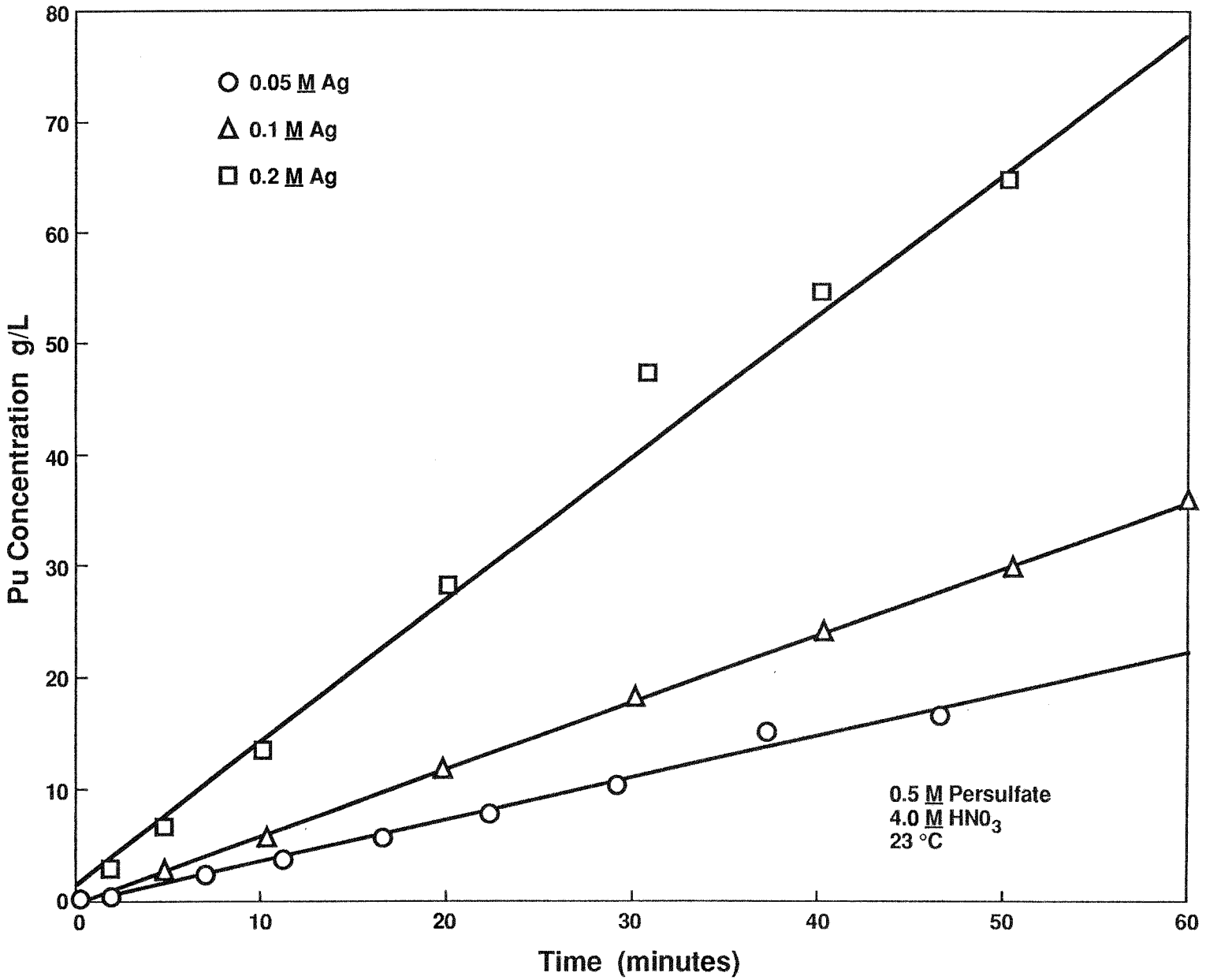
2. Persulfate oxidation of water

$$2S_2O_8^{2-} + 2H_2O = 4HSO_4^{-} + O_2$$

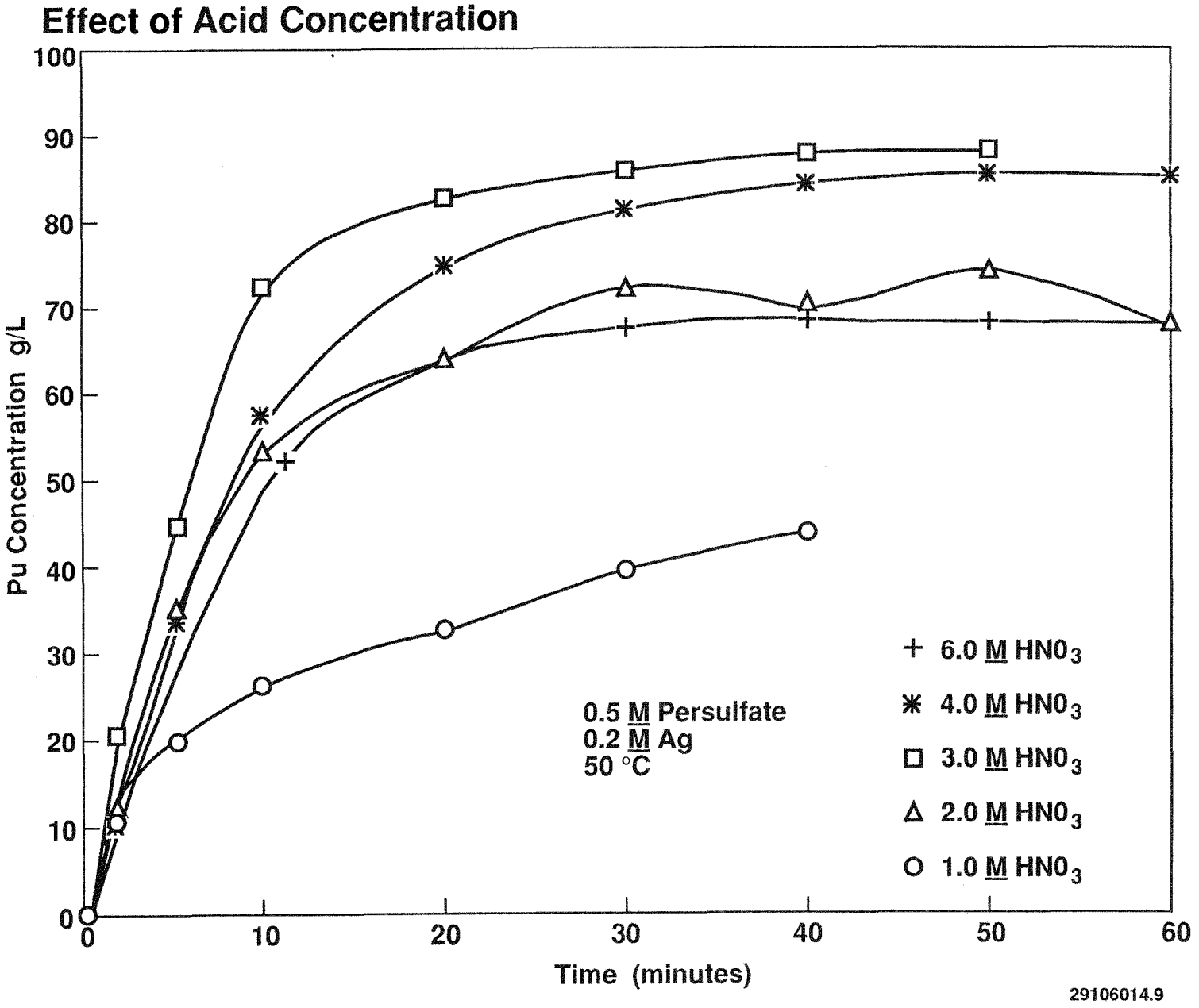
29106014.3


Effect of Persulfate Concentration
○ 0.1 M Persulfate
△ 0.5 M Persulfate
0.05 M Ag
4.0 M HNO3
23 °C
Pu Concentration g/L
Time (minutes)
0
5
10
15
20
0
10
20
30
40
50
60
29106014.7

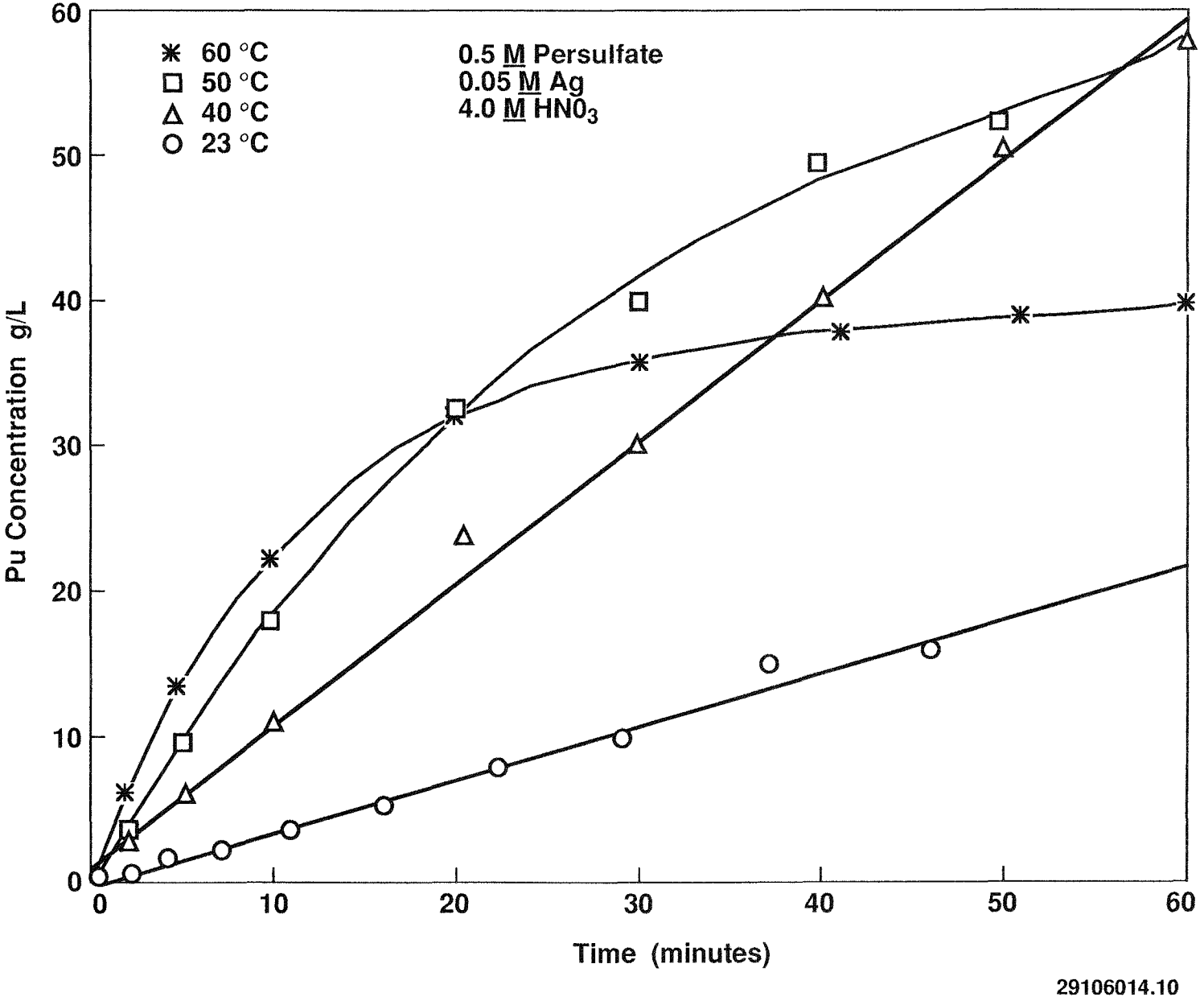
Effect of Silver Concentration



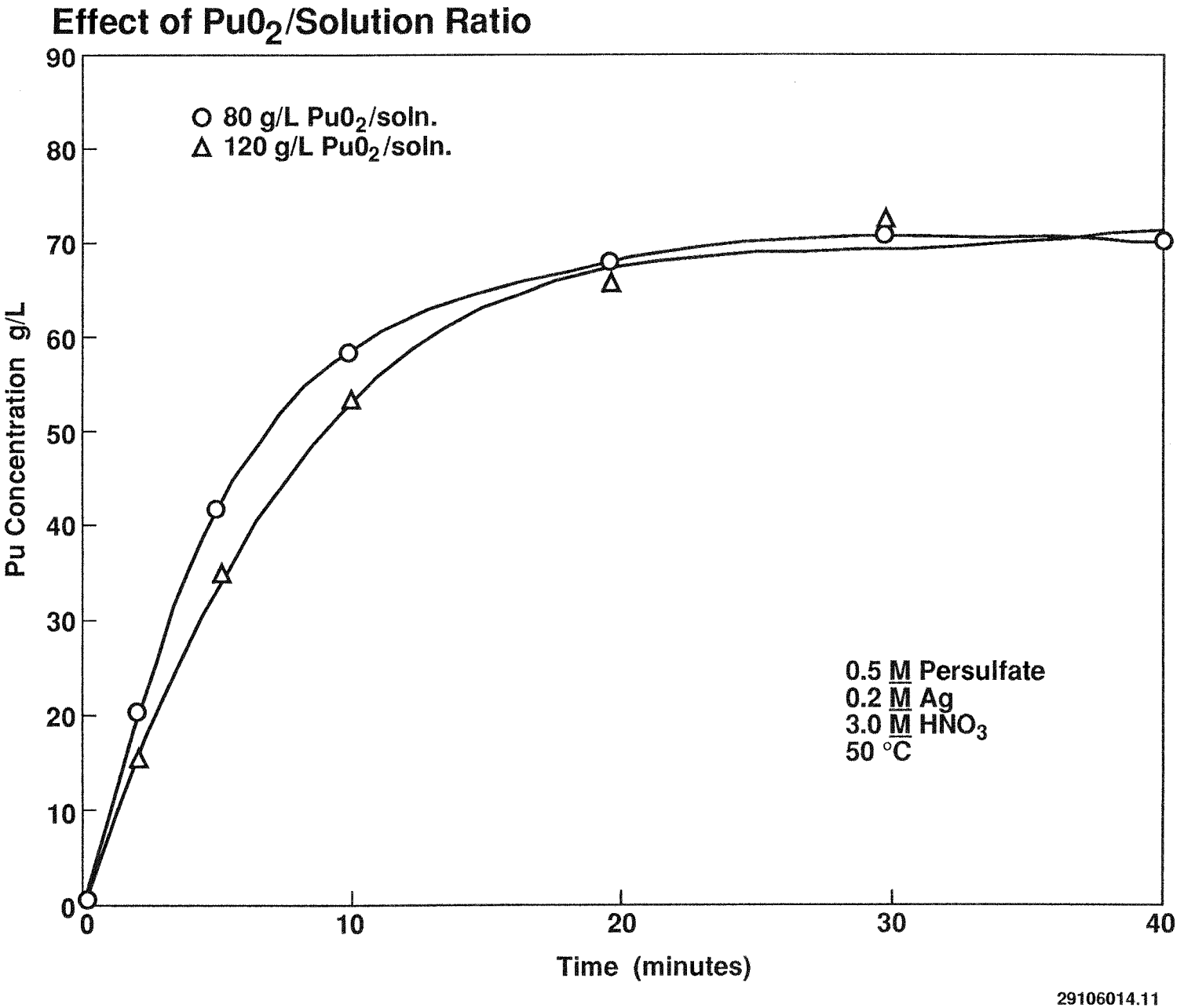
29106014.8


Effect of Acid Concentration
Pu Concentration g/L
Time (minutes)
0
10
20
30
40
50
60
70
80
90
100
0.5 M Persulfate
0.2 M Ag
50 °C
6.0 M HNO3
4.0 M HNO3
3.0 M HNO3
2.0 M HNO3
1.0 M HNO3
29106014.9

Effect of Temperature



29106014.10


Effect of PuO_2/Solution Ratio
○ 80 g/L PuO_2/soln.
△ 120 g/L PuO_2/soln.
0.5 M Persulfate
0.2 M Ag
3.0 M HNO_3
50 °C
Pu Concentration g/L
Time (minutes)
0
10
20
30
40
50
60
70
80
90
29106014.11

Dissolution Reaction Stoichiometry

Temperature °C	Moles $S_2O_8^{2-}$ consumed / Moles Pu dissolved
40	1.33
50	1.38
60	2.99

29106014.4

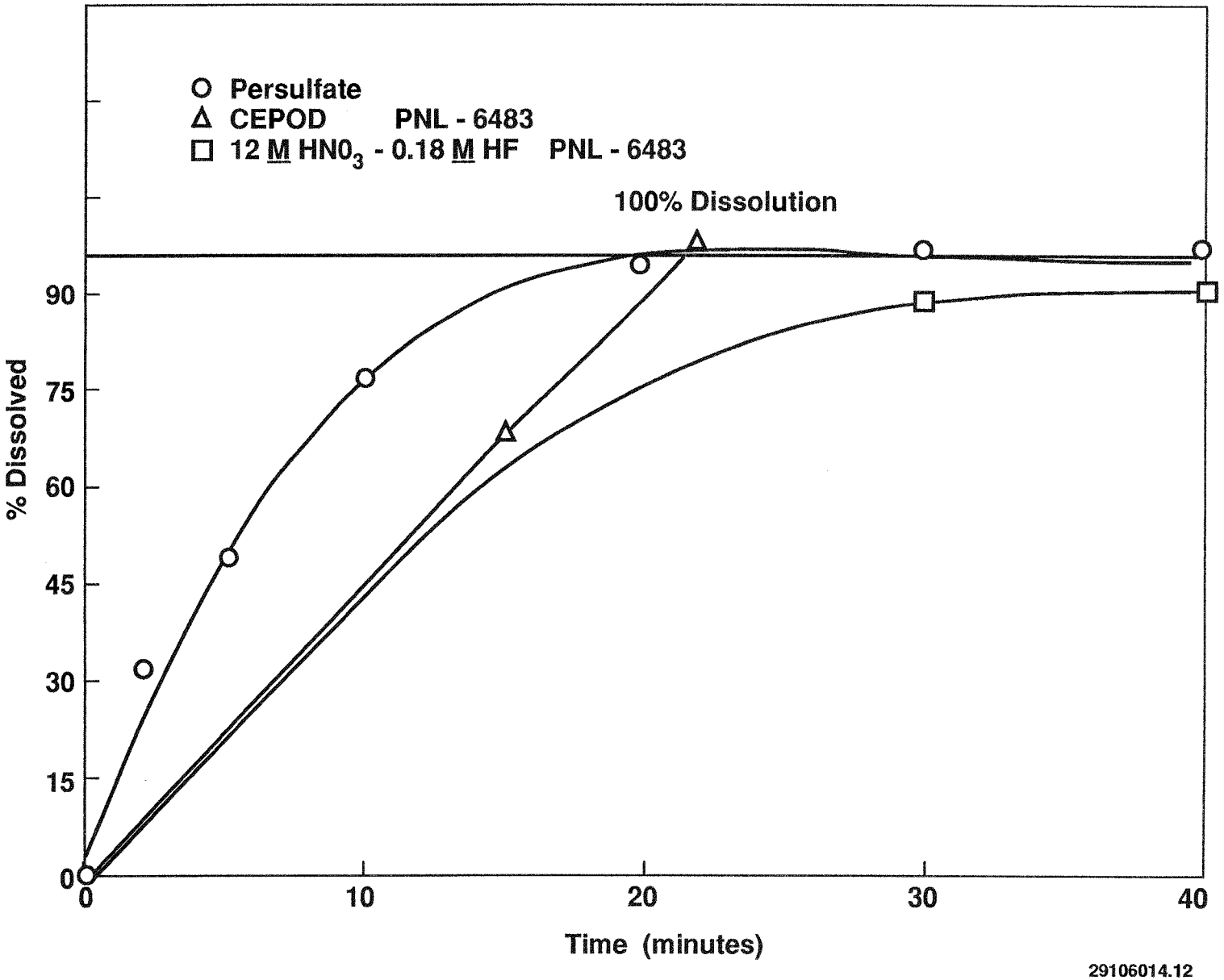
Optimum Dissolution Conditions

Persulfate	0.5M	$K_2S_2O_8/PuO_2 \geq 1.33$
Silver	0.2M	
Nitric Acid	3 M	
Temperature	40 °C*	

* Solutions started at 25 °C often warm themselves to about 40 °C.

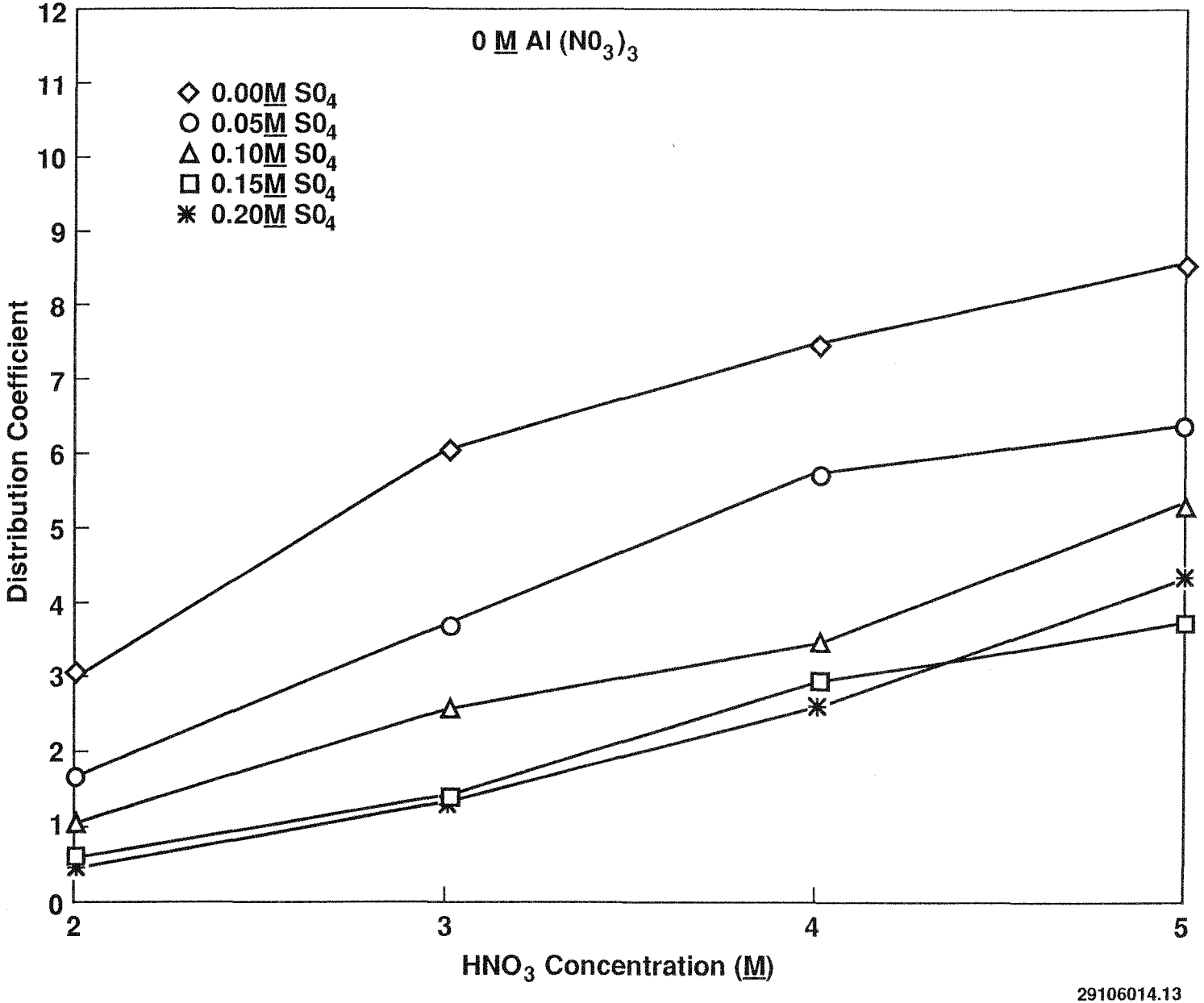
29106014.5

Persulfate vs. CEPOD and Nitric and HF Acids Dissolutions



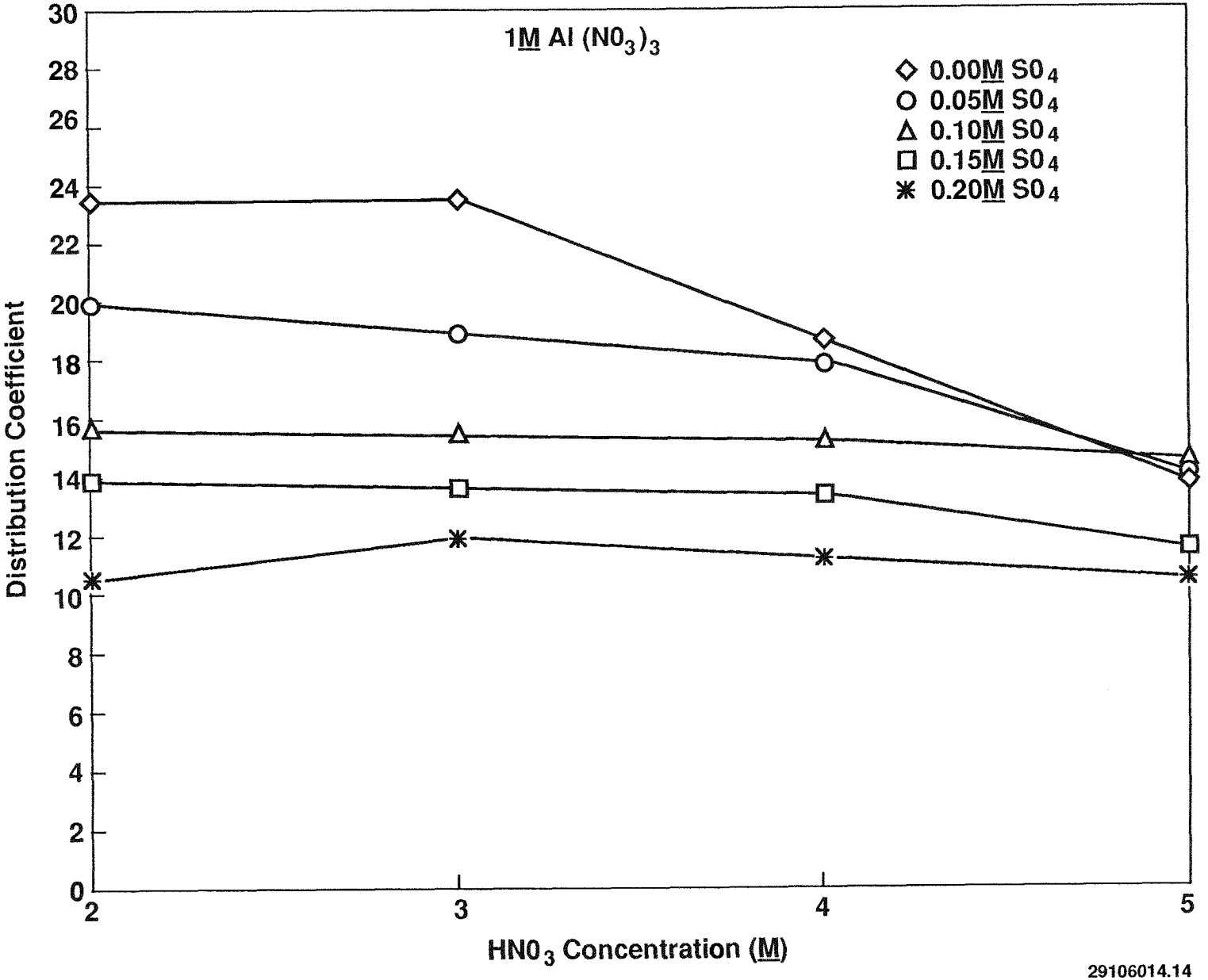
29106014.12

Effect of Sulfate on Extraction of Pu into TBP



29106014.13

Effect of Sulfate on Extraction of Pu into TBP



29106014.14

Leaching from Various Pu-Contaminated Materials

Substrate material	Leach conditions	Pretreatment	Pu Recovery	Product solution
HF Disintegrated HEPA Filter Media	One contact with 0.2 M Ag-0.5 M $K_2S_2O_8$, T = 25 °C	None	89%	Pu(VI)
Polypropylene Filament Wound Filter Media	Same as above	Cut off of core	~90%	Pu(V)
Sand, Slag, and Crucible	Same as above	Ground -200 Mesh, 3 water washes to remove I^-	98.4%	Pu(V)
Z-9 Soil Coarse Fraction	Same as above	Screened +8 mesh	100%, gravel and rocks non-TRU	Pu(VI)
Z-9 Soil Fine	Multiple contacts with 0.2 M Ag-0.5 M $K_2S_2O_8$, T = 25 °C	-200 mesh screen fraction	ca. 80% per contact	Pu(VI)

29106014.6

Conclusion

- Ag - persulfate effective
- More testing planned

29106014.15