Am(VI) Radiolysis

Fuel Cycle Technology

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SUMMARY

This report summarizes activities related to measuring hexavalent Am stability under irradiation conditions for FY17, in completion of FCR&D Milestone M3FT-17IN030103022. The rate at which Am(VI) reduced and Am(V) grew in when exposed to γ-irradiation was measured by UV/Vis spectroscopy in different [HNO_3] and for different total [Am]. These rates were then compared to similar experiments with the added fuel dissolution constituents Ce, U and Zr. Cerium provided radio-protection for Am(VI), U appears to have conferred slight radioprotection, while Zr had no such effect.

CONTENTS

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1. INTRODUCTION

Recently, the autoreduction rates of Am(VI) due to its own radiation have been measured over a range of total Am and HNO_3 concentrations. [1] These data showed that higher Am concentrations resulted in faster reduction rates, due to the generation of HNO_2 and H_2O_2 by Am alpha radiolysis. Thus, in a solution irradiated at higher dose rates, faster reduction of Am(VI) can be expected. In earlier work it was reported that only 2 kGy absorbed dose reduced Am(VI) to Am(V) in a 2 mM total [Am] solution. [2] This is shown in Fig. 1. The pentavalent oxidation state was relatively stable, although higher absorbed doses are expected to also reduce it to Am(III). During FY17 these measurements were continued, across a range of Am and acid concentrations, with Am(VI) radiolytic reduction experiments expected to continue into FY18. The additional experiments performed here were in the presence of Ce(IV), which slows the rate of Am reduction, U(VI) which may have conferred slight radioprotection, and Zr which had no effect. Those results are reported in compliance with the reporting requirements demonstrating completion of milestone M3FT-17IN030103022.

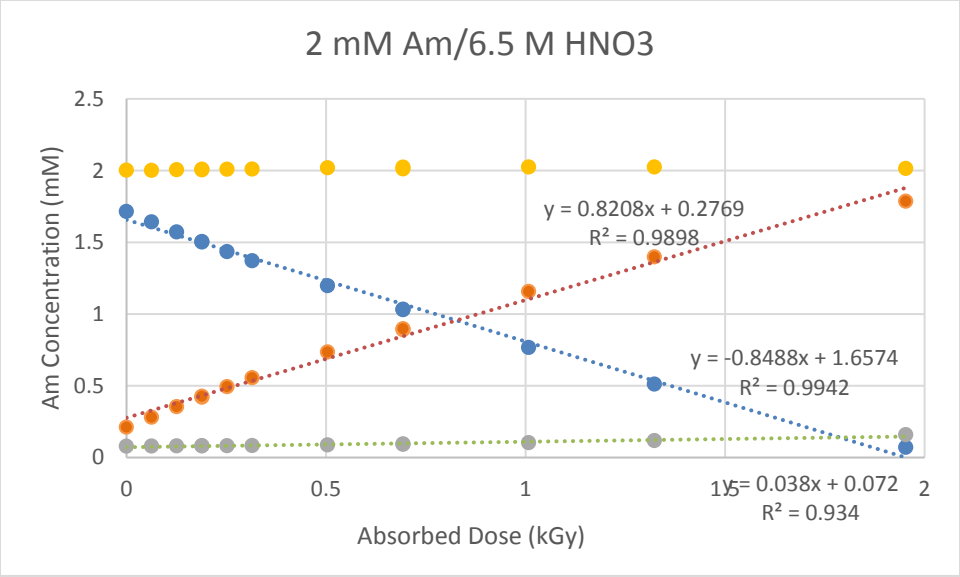

Figure 1. Gamma-ray radiolytic reduction of Am(VI) (blue) in 6.5 M HNO_3, for a total Am concentration of nominally 2 mM, and simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 280 M^{-1} cm^{-1}; Am(V) ε_{718} = 38 M^{-1} cm^{-1}; Am(VI) ε_{999} = 85 M^{-1} cm^{-1}.

2. EXPERIMENTAL

Solutions of varying ^{243}Am concentration were prepared in the appropriate HNO_3 concentrations by dilution of a 2.85 mg mL^{-1} stock solution using standardized nitric acid. These were oxidized using 60 mg mL^{-1} solid sodium bismuthate as described previously. [1] Oxidized solutions were irradiated using a Nordion Gammacell 220E ^{60}Co irradiator at a dose rate of approximately 3.8 kGy h^{-1}. The techniques were originally developed for studies of Np redox chemistry under irradiation and were described previously. [3] The absorbance spectra of the irradiated samples

were collected between absorbed dose increments using a Cary 6000 UV/Vis absorption spectrophotometer. The extinction coefficients of the Am(III) 503 nm peak were those of Zalupski et al [4], and the Am(VI) 999 nm and Am(V) 718 nm peak were determined by mass balance and sensitivity analysis as described by Grimes et al. [1]

3. RESULTS AND DISCUSSION

3.1 Americium in Nitric Acid

The radiolytic reduction of Am(VI) for a 2 mM total [Am] solution is shown in Fig. 2. There it can be seen that the rate of reduction (with respect to absorbed dose rather than time) was about 10 % faster in 3 M HNO_3 than in the higher acid concentration of 6.5 M in Fig. 1. This is in agreement with radiation chemical modeling results reported in [1]. There is essentially no change in the Am(III) concentration, indicating reduction of Am(VI) to Am(V), and the relative stability of Am(V), also in agreement with autoreduction rates. [1]

The UV/Vis spectra for an unirradiated control sample containing 2 mM total [Am] in 3.0 M HNO_3 were collected simultaneously and are shown in Fig. 3, where it is seen that there is no significant autoreduction in the short times during which irradiation experiments are conducted. Autoreduction rates do not confound the radiolytic reduction rates being measured here.

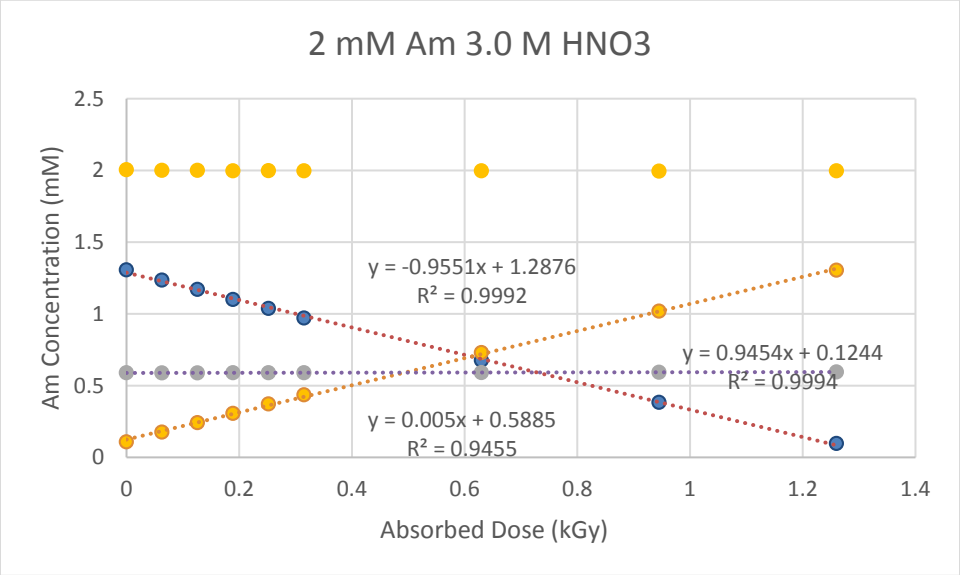

Figure 2. Gamma-ray radiolytic reduction of Am(VI) (blue) in 3.0 M HNO_3, for a total Am concentration of nominally 2 mM, and simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 356 M^{-1} cm^{-1}; Am(V) ε_{718} = 44 M^{-1} cm^{-1}; Am(VI) ε_{999} = 87 M^{-1} cm^{-1}.

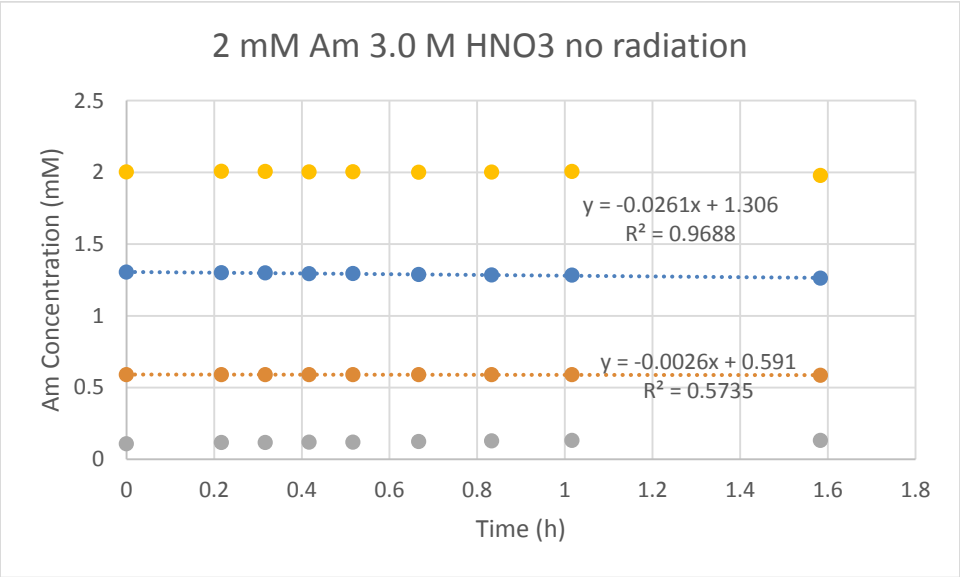

Figure 3. Control sample autoreduction of Am(VI) (blue) in 3.0 M HNO_3, for a total Am concentration of nominally 2 mM, and simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 356 M^{-1} cm^{-1}; Am(V) ε_{718} = 44 M^{-1} cm^{-1}; Am(VI) ε_{999} = 87 M^{-1} cm^{-1}.

Similar data were collected for other total [Am] and [HNO_3] and the absorbed dose-dependent rates are summarized in Table 1. The rate of Am(VI) reduction was equal to the rate of Am(V) generation in all cases, implying a 1-electron reduction as was also reported for autoreduction rates. [1] Although faster reduction was expected at the lower acid concentration, overall rates varied from ~ 0.82 – 1.1 mmol kGy^{-1}, but there was no trend with regard to either $[Am]_{tot}$ or acid concentration. Mean values of -0.900 ± 0.106 mmol kGy^{-1} and 0.893 ± 0.105 mmol kGy^{-1} for Am(VI) and Am(V) respectively, are calculated for this γ-ray dose rate.

Table 1. Rates (mmol kGy^{-1}) for the reduction of Am(VI) and growth of Am(V) in irradiated solution. Gamma-ray dose rate = 3.8 kGy h^{-1}.

HNO_3 (M)	Am_{tot} (mM)	Am(VI) loss	Am(V) growth
3.0	1.0	0.817	0.821
3.0	2.0	0.955	0.954
3.0	4.0	0.816	0.819
6.5	2.0	0.849	0.821
6.5	4.0	1.06	1.05

3.2 Effects of Other Metal Ions

3.2.1 Cerium

The presence of other redox active metal ions or macro-constituents of the fuel dissolution would be expected to affect radiolytic reduction rates for Am(VI), probably via scavenging of produced reducing species. The effect of Ce added at a ratio of 5:1 to Am is shown in Fig. 4. Here, the rate of reduction was slowed by almost a factor of 10. It can also be seen that the ingrowth of Am(V) does not match the loss of Am(VI), and that Am(III) is also growing in. The sum of Am(V) + Am(III) production equals the loss in Am(VI). Thus it is concluded that Ce (present as initially Ce(IV) because of the bismuthate oxidation procedure) provides radioprotection for Am(VI), but that a fraction of produced Am(V) is now reduced to Am(III), possibly by oxidation of Ce(III) by Am(V). These rates are collected in Table 2.

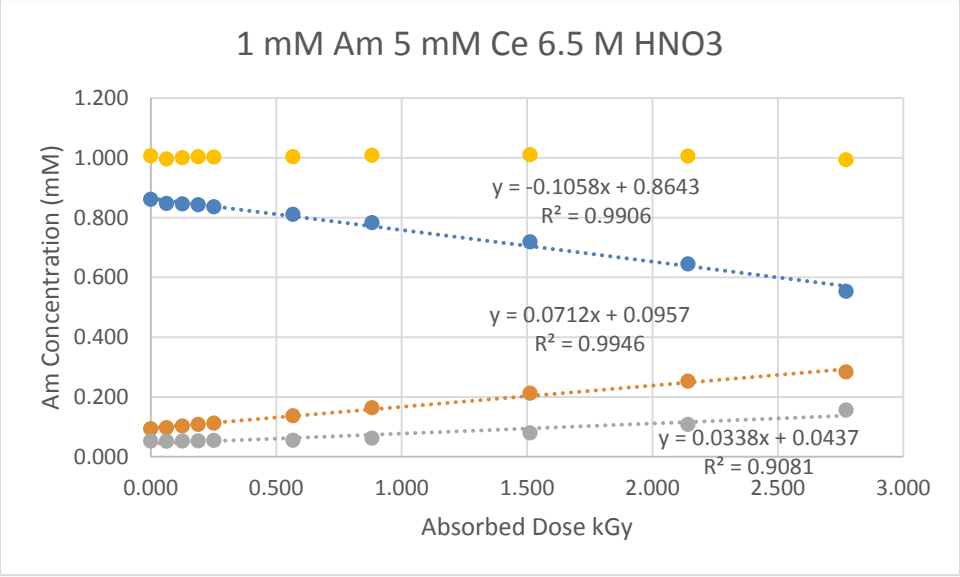

Figure 4. Gamma-ray radiolytic reduction of Am(VI) (blue) in 6.5 M HNO_3, for a total Am concentration of nominally 1.0 mM, in the presence of 5 mM Ce. Simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 356 M^{-1} cm^{-1}; Am(V) ε_{718} = 38 M^{-1} cm^{-1}; Am(VI) ε_{999} = 85.3 M^{-1} cm^{-1}.

Table 2. Rates (mmol kGy^{-1}) for the reduction of Am(VI) and growth of Am(V) and Am(III) in irradiated solution containing other metal ions. Gamma-ray dose rate = 3.8 kGy h^{-1}.

HNO_3 (M)	Am_{tot} (mM)	metal	Am(VI) loss	Am(V) growth	Am(III) growth
6.5	1.00	5 mM Ce	-0.106	0.071	0.033
6.5	1.00	5 mM U	-0.692	0.695	0.022
6.5	1.00	20 mM U	-0.652	0.626	0.027
6.5	1.00	5 mM Zr	-0.809	0.815	0.015

3.2.2 Uranium

Although not considered redox active under fuel cycle conditions, uranium effects on Am(VI) reduction were also investigated since it is a macro-constituent of the fuel dissolution.

Hexavalent Am was irradiated in the presence of 5 mM, and 20 mM U solutions. The results are shown in Figs. 5 and 6, respectively. The reduction rate of Am(VI) and ingrowth of Am(V) were essentially the same at both U concentrations, at -0.672 ± 0.028 mmol kGy^{-1} and 0.661 ± 0.048 mmol kGy^{-1}, respectively. There may have been a slight increase in Am(III). This is slower than the value of ~ 0.9 mmol kGy^{-1} for Am(VI) reduction at this acid concentration in the absence of U (see Table 1). The mechanism by which U would protect Am(VI) is unknown, and replicate data should be collected.

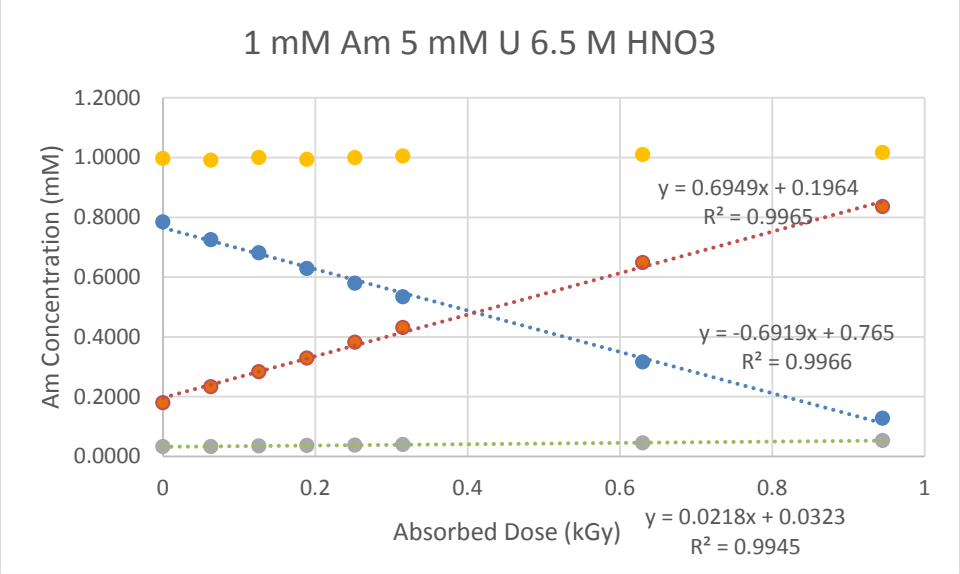

Figure 5. Gamma-ray radiolytic reduction of Am(VI) (blue) in 6.5 M HNO_3, for a total Am concentration of nominally 1.0 mM, in the presence of 5 mM U. Simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 280 M^{-1} cm^{-1}; Am(V) ε_{718} = 42.5 M^{-1} cm^{-1}; Am(VI) ε_{999} = 79 M^{-1} cm^{-1}.

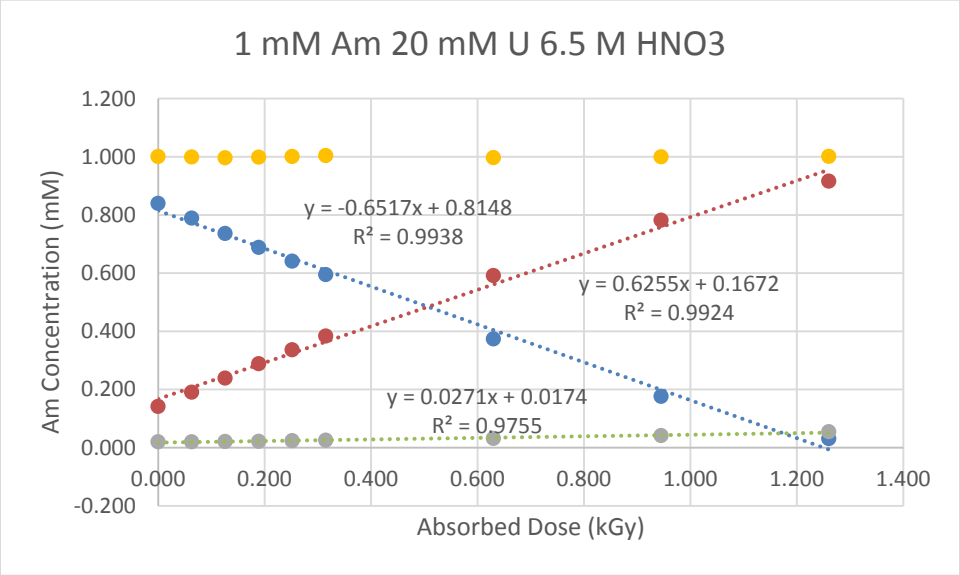

Figure 6. Gamma-ray radiolytic reduction of Am(VI) (blue) in 6.5 M HNO_3, for a total Am concentration of nominally 1.0 mM, in the presence of 20 mM U. Simultaneous change in concentration for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 280 M^{-1} cm^{-1}; Am(V) ε_{718} = 44 M^{-1} cm^{-1}; Am(VI) ε_{999} = 83.5 M^{-1} cm^{-1}.

3.2.3 Zirconium

Zirconium is present in fuel dissolution raffinates in millimolar amounts and as such was investigated here for its effects on Am(VI) radiolytic reduction. As shown in Fig. 7, 5 mM Zr had little effect on Am(VI) reduction. The rate of – 0.809 mmol kGy^{-1} is similar to the -0.900 ± 0.106 mmol kGy^{-1} mean value calculated from Table 1.

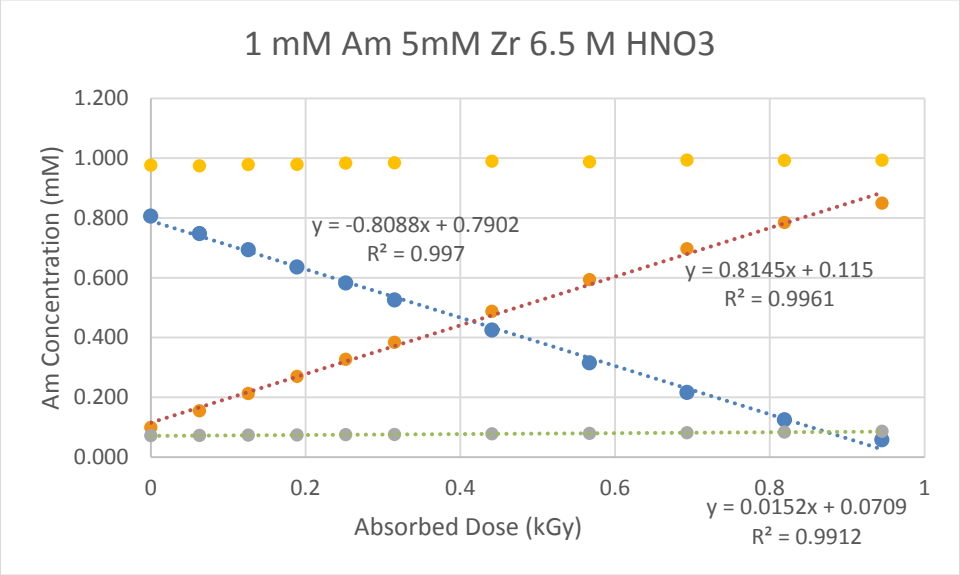

Figure 7. Gamma-ray radiolytic reduction of Am(VI) (blue) in 6.5 M HNO_3, for a total Am concentration of nominally 1.0 mM, in the presence of 5 mM Zr. Simultaneous change in concentration

for Am(V) (orange) and Am(III) (gray). Mass balance for total americium (yellow). Am(III) ε_{513} = 280 M^{-1} cm^{-1}; Am(V) ε_{718} = 38 M^{-1} cm^{-1}; Am(VI) ε_{999} = 71 M^{-1} cm^{-1}.

4. CONCLUSION

Radiolytic reduction rates for Am(VI) were measured across a range of total [Am] and [HNO_3]. Faster rates were expected at 3 M HNO_3, than at 6.5 M HNO_3, based on past modeling. That trend was not identified here, although the data set is limited. Total Am concentration did not affect reduction rates, as expected in the presence of the large externally applied dose rate of 3.8 kGy h^{-1}. Cerium greatly decreased the rate of Am(VI) reduction, while U provided a slight radioprotection effect. Cerium as Ce(IV) was expected to scavenge reducing agents, however, the mechanism of U protection is unknown. Replicate data should be collected to verify the U effect. Zirconium had no influence on Am(VI) reduction rates.

5. REFERENCES

1. Grimes, T.S.; Horne, G.P.; Dares, C.J.; Pimblott, S.M.; Mezyk, S.P.; Mincher, B.J. 2017. Kinetics of the autoreduction of hexavelnt americium in aqueous nitric acid. *Inorg Chem* **56**, 8295-8301.
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4. Zalupski, P.R.; Grimes, T.S.; Heathman, C.R. 2017. Optical absorption characteristics for $^7F_{0'} \rightarrow {}^5L_{6'}$ and $^7F_{0'} \rightarrow {}^7F_{6'}$ transitions of trivalent americium ion in aqueous electrolyte mixtures. *Appl Spectroscopy* DOI 10.1177/000370281772 1528.