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CONCENTRATION OF PLUTONIUM BY CATION EXCHANGE -
STABILIZATION OF Pu(III) IN NITRIC ACID

by

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ABSTRACT

Ascorbic and isoascorbic acids, used in conjunction with sulfamic acid, reduced Pu(IV) rapidly and completely to Pu(III) in solutions of nitric acid. The solutions of Pu(III) were stable. Aminoguanidine sulfate also retarded the oxidation of Pu(III) but did not reduce Pu(IV).

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CONCENTRATION OF PLUTONIUM BY CATION EXCHANGE - STABILIZATION OF Pu(III) IN NITRIC ACID

INTRODUCTION

Plutonium can be conveniently concentrated by absorption on a bed of cation exchange resin followed by elution with a small volume of concentrated nitric acid. The process is most efficient when the plutonium is kept in the trivalent state⁽¹⁾. Stabilizing compounds, such as sulfamic acid and aminoguanidine sulfate, retard the oxidation of Pu(III) even in solutions that contain 6M nitric acid, so that only a few per cent of the plutonium is oxidized in several days. These solutions are usually stable enough to be used in processes which require plutonium in the trivalent state. On rare occasions, however, sulfamic acid completely fails to repress the oxidation of Pu(III) by nitric acid during the elution step. When the Pu(III) is oxidized rapidly, gases are evolved in the resin bed. The gassing is sometimes sufficiently vigorous to disrupt and channelize the bed. Oxidation of Pu(III) during storage of the eluate is also a problem because for some uses very little Pu(IV) can be tolerated and the rate of oxidation must be retarded even more than can be accomplished by sulfamic acid alone.

The present study was made to define the limits of effectiveness of sulfamic acid and to find better stabilizers.

SUMMARY

The effectiveness of stabilizers, such as sulfamic acid, in retarding the oxidation of trivalent plutonium, is influenced by the temperature and by the concentrations of plutonium, nitric acid, and nitrous acid. The relative importance of these factors was studied by using Fe(II) as a stand-in for Pu(III). The studies with iron showed that many compounds that contain amine, amido, or imino groups act as stabilizers; aminoguanidine sulfate was as effective as sulfamic acid. The oxidation of Pu(III) stabilized with sulfamic acid was slow; it was retarded most effectively by adding ascorbic acid or isoascorbic acid, and was retarded significantly by adding aminoguanidine sulfate. The ascorbic acids effected rapid and complete reduction of the Pu(IV) that formed during storage in partially stabilized solutions of nitric acid; for such use as reductants, the ascorbic acids were unique among all of the additive compounds that were evaluated.

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DISCUSSION

GENERAL BACKGROUND

THE CATION EXCHANGE PROCESS

Trivalent plutonium in nitric acid is absorbed by a resin of the sulfonic acid type according to the following reaction

The plutonium can be absorbed from dilute (0.50M) nitric acid, and eluted by strong (6M) acid. A typical process cycle for concentration and purification consists of four steps.

- (1) Feed Absorption - Plutonium that has been reduced to the trivalent state by a reductant such as hydroxylammonium sulfate (0.05M) is absorbed from a dilute solution. The excess of hydroxylammonium ions is also absorbed.
- (2) Uranium Elution - Uranium and some fission products are eluted with 0.25M sulfuric acid; this treatment does not elute the Pu(III).
- (3) Product Elution - The plutonium is eluted with strong nitric acid (5.7M), which is prevented from oxidizing the plutonium by a stabilizer such as sulfamic acid (0.3M).
- (4) Reconditioning - The column is prepared for the next process cycle by flushing with dilute nitric acid (0.1M).

NATURE OF THE CHEMICAL REACTIONS

Retardation of Oxidation

The oxidation of Pu(III) by nitric acid is retarded by compounds which react with nitrous acid. The oxidation proceeds through a chain of reactions, in which nitrous acid has an important part. The apparent oxidation reaction is

If this reaction is permitted to proceed, the reaction soon becomes very rapid because it is autocatalytic^(5,10). The nitric oxide formed during the oxidation produces nitrous acid which is a catalyst for the oxidation reaction, (1a). The nitrous acid is formed according to reaction (1b)

The function of a stabilizer is to react with nitrous acid as rapidly as it is formed so that the oxidation of Pu(III) is prevented or proceeds only very slowly. Rapid oxidation of plutonium occurs when the rate of formation of nitrous acid exceeds the rate of its destruction, and the chain of reactions becomes autocatalytic.

Sulfamic acid and aminoguanidine sulfate react rapidly and completely with nitrous acid, and thereby slow the chain of oxidation reactions. The reactions between nitrous acid and sulfamic acid or aminoguanidine sulfate yield either soluble products or gases. The course of the reaction depends on the concentrations of the reactants and on the temperature⁽³⁾. If rapid reactions occur and the stabilizers are completely destroyed, the over-all reactions are⁽²⁾

Nitrogen oxides are formed when the nitric acid is reduced by Pu(III) as in reaction (1a). If oxidation occurs slowly, the nitrous acid merely combines with the amine and imino groups⁽³⁾.

If reaction (4) only goes as far as the addition step, gas is not formed. Aminoguanidine sulfate, which contains two amine and two imino groups, potentially could react with four mols of nitrous acid.

Reduction with Ascorbic Acid

Ascorbic acid, in the presence of sulfamic acid, reduces Pu(IV) to Pu(III) even in the ion exchange eluate which contains 4.7M nitric acid. In the absence of sulfamic acid, the ascorbic acid is immediately oxidized by the nitric acid. Titration of ascorbic acid with potassium iodate or iodine showed that the reduction by ascorbic acid proceeded by the transfer of two electrons. The reaction is probably^(4,6)

Ascorbic Acid

Dehydro-ascorbic acid

Isoascorbic acid, which reacts similarly, is as effective as ascorbic acid.

RAPID OXIDATION OF Pu(III) IN RESIN BEDS

Source of Information

In the following paragraphs, information from pertinent ion exchange experiments has been summarized to clarify the conditions required to avoid rapid oxidation of Pu(III) by nitric acid during the elution step of the cation exchange process. The runs upon which the statements are based were made for various purposes, and the data will be presented in greater detail in a subsequent report.

Summary of Conditions Required

Rapid oxidation takes place when a sufficiently high temperature and high concentrations of nitric acid, nitrous acid, and plutonium are attained in the resin bed during the elution. Precise limits on the requirements are difficult to establish because many variables must be considered simultaneously, but the reaction can be understood better by studying the data that are available. The concentration of plutonium in the eluate depends directly on (1) the concentration of nitric acid in the elutriant, (2) the initial concentration of absorbed plutonium in the resin, and (3) the time of contact of resin with elutriant. The concentration of nitric acid must be at least 4.7M to elute the Pu(III) from the resin bed at the desired high concentrations. Since nitrous acid appears to catalyze the oxidation reaction, the nitric acid that is used should be free from nitrous acid. Because operation at elevated temperatures would decrease the effectiveness of the stabilizer, the exchange columns are usually operated at room temperature.

Limits on Concentration of Nitric Acid

The maximum concentration of nitric acid that can be used without oxidizing the Pu(III) depends on the depth of resin loaded with plutonium. With elutriants stabilized with 0.30M sulfamic acid, 4.7M nitric acid is the maximum concentration that can be used without the occurrence of oxidation when the bed is loaded to a depth of 35 cm. The concentration of nitric acid can be increased to 5.7M without the formation of gas when the bed is loaded only to a depth of 25 cm. The same concentrations of plutonium are obtained in the eluate with either elutriant. Elutriant containing 6.7M HNO₃ generates gas even in a bed 15 cm deep. In these experiments the resin was loaded during the absorption step so that 75% of the total exchange capacity of the loaded resin was occupied by plutonium, and the flow rate of elutriant was 0.50 ml/(min)(cm²).

Limitation by Increasing Flow Rate

Gassing can be prevented by increasing the flow rate during elution, but the concentration of plutonium in the eluate decreases as the flow rate of the elutriant is increased. When 6M elutriant* is used, and the bed is loaded 25 cm deep with 75% of its exchange capacity occupied by plutonium, the peak concentrations of plutonium are 145 and 122 g/l at 0.50 and 1.0 ml/(min)(cm²), respectively. This mode of limitation of gassing apparently depends on the lowering of the peak concentration of plutonium that is attained during the elution.

Oxidation of Pu(III) in the resin bed can be stopped even after the reaction has started if the flow rate of the elutriant is increased several fold. At the higher flow rate the reacting eluate is rapidly chilled by being swept into cooler portions of the resin bed, and at the same time the concentration of plutonium in the freshly produced eluate is decreased.

SLOW OXIDATION OF Pu(III) IN THE ELUATE

Initial State of the Eluate

The plutonium in the eluate from the ion exchange resin is almost completely in the trivalent state, but slow oxidation to the tetravalent state starts immediately even when sulfamic acid is present. A typical eluate initially has the following composition.

50 to 60 g Pu(III) per liter
4.7M nitric acid
0.30M sulfamic acid
0.35M hydroxylamine nitrate

This solution contains both oxidizing and reducing chemicals. The sulfamic acid slows down the reactions in the oxidation chain and keeps the chemicals in a slowly changing "pseudo-equilibrium".

Rate of Slow Oxidation

The progress of the oxidation of Pu(III) is shown in Figure 1 for an eluate produced by using a solution containing 5.7M nitric acid and 0.30M sulfamic acid as the elutriant in the over-all procedure described in Reference (1). The Pu(III) was oxidized at the rate of approximately 5 to 6% per day until about 42% of the plutonium was in the tetravalent state, and then the rate of oxidation decreased to less than 1% per day.

*5.7M HNO₃ plus 0.3M sulfamic acid

FIGURE 1 - SLOW OXIDATION OF Pu(III) TO Pu(IV) IN ION EXCHANGE ELUATE

STUDY OF THE OXIDATION REACTIONS THAT CAUSE GASSING

CONDITIONS REQUIRED FOR RAPID OXIDATION

Fe(II) as "Stand-in" for Pu(III)

The course of the oxidation of Pu(III) cannot be followed easily, so the study of the gassing problem was made with Fe(II) instead of Pu(III). Fe(II) is a reasonably good "stand-in" for Pu(III); the oxidation potential of the Fe(II) - (III) couple is 0.77 volt while that of the Pu(III) - (IV) couple is 0.97 volt. The stages of reaction observed during the oxidation of Fe(II) closely parallel the stages observed during experiments made with Pu(III).

Experimental Procedure

Fifty ml of elutriant (5.7M nitric acid and 0.30M sulfamic acid) was placed in a 500-ml 3-neck flask which contained a stirrer and a thermometer. Solid ferrous sulfate which dissolved immediately was added, and the solution in the flask was slowly heated, at about 1°/min, in a water bath. Samples of the solution were taken when various temperatures were reached, and the residual concentrations of Fe(II) were determined. The rate of gas evolution during the course of the reaction was estimated visually. The maximum temperature to which the solution could be heated before rapid reaction occurred was a useful

index of the effectiveness of the stabilizer under the conditions that were used in the test. The temperature at which rapid reaction occurred could be reproduced within $\pm 2^{\circ}\text{C}$ when the same stock of nitric acid was used. The amount of dissolved nitrogen oxides present in nitric acid from different sources varied. For the work described in this report, the same stock of nitric acid was used in all of the experiments in each series of related tests.

Changes in Rate Observed During Oxidation

The changes in the rate of oxidation as the temperature was raised are shown by Figure 2. During the first period, Fe(II) (green) was slowly oxidized to Fe(III) (brown) without the evolution of gas. During the second period, small bubbles of gas collected on the walls of the flask. During the third period, which was reached at a definite and reproducible temperature, the remaining Fe(II) oxidized suddenly to Fe(III) with rapid evolution of gas.

The concentrations of Fe(III) were determined colorimetrically. The color developed with orthophenanthroline was measured at a wavelength of 505 m μ on a Beckman Model D spectrophotometer.

FIGURE 2 - OXIDATION OF Fe(II) BY NITRIC ACID STABILIZED WITH SULFAMIC ACID

Composition of Gases Evolved

The gas evolved during slow oxidation of Fe(II) by 5.7M nitric acid and 0.30M sulfamic acid was collected and found by analysis in a mass spectrometer to contain about 98 mol % nitrogen and less than 0.5 mol % nitrous oxide. The gas evolved during the rapid oxidation of Fe(II) which was absorbed on a bed of "Dowex" 50-X12 contained 90% nitrogen and 10% nitrous oxide. This composition is only approximately correct since there probably was some reaction of the nitrogen oxides with air initially present in the bed and some separation due to the differences in the solubilities of the nitrogen and the oxides in the reacting solution.

Catalytic Effect of Nitrous Acid

The temperature at which the stabilizer failed was significantly lowered by the presence of nitrous acid due to catalytic acceleration by nitrous acid of the oxidation of the Fe(II). If the nitric acid used in the experiments had been stored in a partially filled bottle and exposed to light, oxides of nitrogen formed and rapid oxidation occurred at a lower temperature than if pure water-white acid were used. When 15M nitric acid which contained 0.1% by weight of N_2O_3 was used to prepare the test solution, reaction occurred below 24°C, whereas when pure nitric acid was used under the same conditions rapid oxidation did not occur below 40°C. Sulfamic acid was not a sufficiently effective stabilizer to suppress the effect of the nitrogen oxides.

Effect of Nitric Acid Concentration

Data obtained in other studies have shown that the effectiveness of stabilizers in Pu(III) solutions is greatly decreased as the concentration of nitric acid is increased; the same dependence on acid concentration was found in experiments made with Fe(II). When, in a solution stabilized with 0.30M sulfamic acid, the initial concentration of Fe(II) was 0.40M and that of nitric acid was 3.5M, the solution did not react rapidly even at 100°C, although gas was evolved slowly and all the Fe(II) was eventually oxidized. When the concentration of nitric acid was increased to 4.0M in a similar solution, rapid reaction started at 40°C.

Effect of Iron Concentration

Data obtained in other studies have also shown that the effectiveness of stabilizers in Pu(III) solutions is greatly decreased when the peak concentrations of plutonium during the elution step are high; a similar dependence on Fe(II) concentration was found. These experiments were made with the elutriant used in the cation exchange process, 5.7M nitric acid and 0.30M sulfamic acid. Rapid reaction occurred at 24°C when the concentration of Fe(II) was 0.40M, which corresponds on a molar basis to 96 g Pu/l. The highest peak concentrations of plutonium

that have been attained without rapid oxidation in small diameter columns, which would be well cooled, were about 160 g Pu/l, or 0.68M; therefore, the similarity to the results of the iron test is reasonably close. In the iron experiments, solid ferrous sulfate was dissolved in the elutriant and the solutions were heated at about 1°/min. As shown in the following table, (1) the temperatures at which the first gas bubbles were observed, (2) the temperatures at which the stabilizer failed, and (3) the interval between these two temperatures, all decreased when the concentration of Fe(II) was increased. These data are also shown in Figure 3.

Effect of the Concentration of Iron on the
Effectiveness of Sulfamic Acid as a Stabilizer

Solution: 5.7M Nitric Acid and 0.30M Sulfamic Acid

Initial Conc of Fe(II), M	T ₁ , Temp at Which Initial Gas Bubbles Appeared, °C	T ₂ , Temp at Which Rapid Oxidation Occurred, °C	ΔT, (T ₂ -T ₁), °C
0.1	56	>90*	>34
0.2	42	48	6
0.4	24	28	4
0.5	19	21	2

*No rapid reaction when heated to 90°C

FIGURE 3 - EFFECT OF IRON CONCENTRATION ON OXIDATION OF Fe(II)
IN NITRIC ACID - SULFAMIC ACID SOLUTIONS

SCREENING TESTS OF ALTERNATIVE STABILIZERS

Scope of Tests

Fourteen compounds were tested to determine their effectiveness for retarding the oxidation of Fe(II) by nitric acid. These compounds were selected because they had been reported to destroy nitrous acid, or the compounds contained groups known to react with nitrous acid.

Experimental Procedure

The relative rates of oxidation were indicated by gas evolution which was estimated visually. About 0.30 mol of the test compound was added per liter of 5.7M nitric acid. Then 0.40 mol of solid ferrous sulfate was added per liter and dissolved. The solution was then heated at about 1°/min on a water bath. The experiments were made with 50 ml of solution.

Summary of Results

The best results were obtained with aminoguanidine sulfate which in a subsequent experiment was about as effective as sulfamic acid for stabilizing Pu(III) during the elution step of the cation exchange process. Many of the compounds tested failed to prevent rapid oxidation even at room temperature. Most of the compounds that were effective as stabilizers also reduced Fe(III) to Fe(II); this reaction was taken as an additional indication⁽⁷⁾ that these compounds could retard the oxidation of Pu(III).

The results of the screening tests, summarized in the following table, indicate that best stabilization was obtained with compounds that contained amino, imino, and imido groups. The other compounds that were tested because they had been reported to destroy nitrous acid failed as stabilizers because their reaction was either not rapid enough or not complete enough to retard the oxidation of Fe(II).

In later work it was discovered that ascorbic acid was an excellent reducing agent for plutonium even in nitric acid if sulfamic acid were present, and that the plutonium would be held in the trivalent state if ascorbic acid were present. Ascorbic acid was not tried during the screening tests.

Screening Tests of Compounds
With Potential Stabilizing Action

Composition of test solution: 5.7M Nitric Acid
0.3M Test Compound
0.4M Ferrous Sulfate
Temperature: 23°C

Test Compound	Active Groups	Relative Rate of Oxidation of Fe(II)	Reducing Action on Fe(III) in Nitric Acid	
			Conc, HNO ₃ , M	Relative Degree Reduction
Aminoguanidine sulfate	Two Amino Two Imino	None Apparent	5.0	Complete ^a
Nitroacetanilide	One Imino	None Apparent	5.0	Complete
Succinyl hydrazine	Two Imino	Slow	5.0	Partial
Thiourea	Two Amino	Slow	-	-
Acetonitrile	One Imido	Slow	5.0	Partial
Succinonitrile	One Imido	Slow	5.0	Partial
Furoic acid	Keto-Acid	Rapid	0.5	Partial
Furion	Keto Aldehyde Keto Alcohol	Rapid	0.5	Partial
Methylalpha-D-glucoside	Keto Alcohol	Rapid	0.5	None ^b
2-Picoline	One Imido	Moderate	0.5	None ^b
Propiolactone	Unsaturated Ketone	Rapid	0.5	None ^b
L-sorbose	Keto Alcohol	Rapid	0.5	None ^b
Sorbitol ^c	Poly Alcohol	Instantaneous	0.5	None ^b

^aFe(III) was slowly reduced, but Pu(IV) was not reduced in 24 hours

^bBased on visual color change within 5 minutes

^cIntermediate compound for preparation of ascorbic acid

VALENCE STABILIZATION WITH AMINOGUANIDINE

ADDITIONAL TESTS WITH Fe(II)

In confirmation of the scouting tests, aminoguanidine sulfate was found to be much more effective than sulfamic acid as a stabilizer for Fe(II). No rapid oxidation occurred even at 90°C when a solution containing 1M ferrous sulfate, 5.7M nitric acid, and 0.30M aminoguanidine sulfate was heated. The Fe(II) was oxidized slowly with little evolution of gas. After 1.5 hours at 95°C, the iron was completely oxidized, but no violent reaction had occurred. In a similar test with a solution containing only 0.5M ferrous sulfate and 0.30M sulfamic acid, rapid oxidation occurred at 21°C.

PREVENTION OF RAPID OXIDATION OF PLUTONIUM IN RESIN BEDS

In an experiment with Pu(III), aminoguanidine was only slightly better than sulfamic acid. An elutriant consisting of 5.7M nitric acid and 0.3M aminoguanidine sulfate was used to elute plutonium from a 14-inch-deep bed of "Dowex" 50-X12 which had been loaded to saturation with a solution that occupied 75% of the exchange capacity of the bed with plutonium. When about one-third of the plutonium had been eluted, gas bubbles formed in the liquid above the resin. An increase in the flow rate of the elutriant stopped the evolution of gas, and rapid oxidation did not occur. In similar experiments in which the elutriant was 5.7M nitric acid and 0.3M sulfamic acid, one experiment was completed successfully, but during the second experiment violent gassing occurred and could not be stopped.

The difference between the behavior of Fe(II) and that of Pu(III) is probably due to the higher potential of the plutonium couple. Fe(III) was completely reduced by aminoguanidine sulfate whereas Pu(IV) was not reduced after 24 hours.

RETARDATION OF SLOW OXIDATION IN ELUATE

Purpose

Although the plutonium in the eluate from cation exchange resin normally is almost completely in the trivalent state, slow oxidation to the tetravalent state starts immediately after elution even when sulfamic acid is present. A stabilizer was sought that would preserve the plutonium entirely in the trivalent state.

Experimental Procedure

The course of the oxidation reaction was followed by sampling the eluate at the times indicated and determining the valence states of the plutonium. The fractions of the total plutonium that were in each valence state were determined by spectrophotometric analyses. For a few samples, the analyses were confirmed by extracting the tetravalent plutonium with thenoyltrifluoroacetone, TTA; the rest of the plutonium was assumed to be in the trivalent state. The results obtained by the two analytical methods were essentially the same. No Pu(V) or Pu(VI) was detected spectrophotometrically.

Summary of Results

Aminoguanidine sulfate further retarded the slow oxidation of Pu(III) in a solution prepared by elution from a resin column with 5.7M nitric acid and 0.30M sulfamic acid. The amount of retardation was found to be proportional to the concentration of the aminoguanidine added as shown below:

Effect of the Concentration of Aminoguanidine Sulfate Upon Stabilization

(Same batch of eluate was used for all runs)

Molarity of Aminoguanidine Sulfate in Eluate	Pu(III) in Eluate, Days after Elution, %					
	Fresh	1 Day	2 Days	3 Days	4 Days	6 Days
0 (Control)	100	-	81	-	-	-
0.1	100	97	92	89	82	76
0.2	100	97	92	89	86	82
0.3	100	97	93	90	88	84

The effect of the stabilizer on partially oxidized plutonium was determined by adding one mol of aminoguanidine sulfate per liter to the control sample on the third day after elution. At the end of six days, 81% of the plutonium was still trivalent; none of the Pu(IV) had been reduced. This result indicates that, like sulfamic acid, aminoguanidine stabilizes plutonium in the trivalent state, but that it does not reduce Pu(IV) to Pu(III).

VALENCE STABILIZATION WITH ASCORBIC ACID

REDUCTION OF Pu(IV) IN NITRIC ACID

Pu(IV) can be reduced to Pu(III) by ascorbic acid in a few minutes if 0.1 to 0.3 mol of sulfamic acid per liter of solution is present to

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prevent oxidation of the ascorbic acid by the nitric acid. One half mol of ascorbic acid per mol of Pu(IV) plus 0.05 to 0.10 mol per liter in excess is required for the reduction.

RETARDATION OF SLOW OXIDATION IN ELUATE

Summary of Result

Ascorbic acid also will retard the slow oxidation of the plutonium solution in eluate containing 4.7M nitric acid and 0.3M sulfamic acid. Any plutonium that already has been oxidized will be reduced when the ascorbic acid is added. In solutions stabilized with ascorbic acid, all the plutonium remained in the trivalent state for at least three days after elution, and then oxidation proceeded at a very slow rate as shown below.

Effect of Concentration of Ascorbic Acid upon Stabilization

(Same batch of eluate was used for all runs)

<u>Molarity of Ascorbic Acid</u>	<u>Pu(III) in Eluate, Days after Elution, %</u>					
	<u>Fresh</u>	<u>1 Day</u>	<u>2 Days</u>	<u>3 Days</u>	<u>6 Days</u>	<u>7 Days</u>
0 (Control)	100	97	90	84	72	69
0.2	100	100	100	100	97	98
0.3	100	100	100	100	97	-

Storage of Ascorbic Acid Solutions

Approximately one-molar solutions of ascorbic acid in water or in 0.1 to 0.2M nitric acid did not decrease in reducing strength over a 14-day period. Although the solutions turned light brown after three days, their reducing normality was not significantly affected. The presence of a piece of stainless steel in a solution containing 0.1M nitric acid did not affect the stability of the ascorbic acid. Ascorbic acid is stable in acid or neutral solutions but not in alkaline solutions⁽⁴⁾. The decomposition of ascorbic acid is catalyzed by some metallic ions, e.g., copper⁽⁴⁾.

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