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A STUDY OF THE EXPLOSIVE PROPERTIES OF
URANIUM-ZIRCONIUM ALLOYS

by

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A STUDY OF THE EXPLOSIVE PROPERTIES OF URANIUM-ZIRCONIUM ALLOYS

by

Robert P. Larsen, Roberta S. Shor
Harold M. Feder and D. Stanley Flikkema

I. SUMMARY

The explosion of uranium-zirconium alloys on treatment with nitric acid has been investigated. The cause of the explosion has been clarified and its mechanism ascertained. The existence of the epsilon phase, a hitherto questionable feature of the uranium-zirconium phase diagram, has been verified.

The prevention of explosions during pickling, etching or dissolution of these alloys has been studied; recommendations are made for safe handling. An unclassified safety film on this subject is available for distribution to interested laboratories.

II. CONCLUSIONS

The following conclusions have been drawn from the experimental studies reported here.

1. The existence of the epsilon phase in the U-Zr system has been verified by chemical methods and X-ray diffraction.
2. Depending on composition, homogeneity and previous thermal history uranium-zirconium alloys with 1 to 50 w/o zirconium contain lesser or greater fractions of finely divided epsilon phase in a matrix of alpha-uranium. On treatment with nitric acid the matrix is rapidly dissolved and the epsilon phase is slowly oxidized. This oxide is a solid solution of urania and zirconia in a mole ratio of approximately one to three. In the course of such acid treatment, or subsequently, the unoxidized particles of the epsilon phase may undergo a rapid oxidation with explosive violence.
3. The explosion may be prevented by increasing the rate of solution of the minor phase by the addition of fluoride ion.

997-004

III. INTRODUCTION

Several laboratories have reported the occurrence of explosions during the pickling or etching of zirconium-uranium alloys.^(1,2,3) An investigation was undertaken at Argonne to study the mechanism of the explosion and to formulate a set of conditions which would eliminate the explosion hazard when such alloys are pickled, etched, or completely dissolved in nitric acid media.

IV. EXPERIMENTAL STUDIES OF THE EXPLOSION MECHANISM

It was observed at the outset that the 2 w/o alloy did not dissolve cleanly in nitric acid. The residues contained both zirconium and uranium and were impervious to nitric acid leaching. Furthermore, it was observed that dangerous explosions did occur during the course of nitric acid attack on this metal.

A. Occurrence of Explosions in Nitric Acid

Explosions have been reported during the attack of nitric acid on alloys containing as little as 1 w/o⁽¹⁾ zirconium and as much as 30 w/o.⁽³⁾ Studies in this Laboratory have shown that a black surface coating forms on the metal during the reaction and that, in this condition, explosions may take place either spontaneously or as the result of mechanical shock or friction from contact with the container wall. Similar, but less violent, explosions also take place when dried samples of the partially reacted metal are sparked or struck in air. It has been observed that alloy composition, surface area, thermal history, duration of acid treatment, concentration of acid, and temperature are variables that determine the vigor of the reaction. The effect varies from a "bump" to an explosion characterized by a loud report, a bright flash and a force sufficient to eject the acid and shatter a heavy glass container. Figures 1 and 2 are sequences taken from high speed and standard motion pictures of some explosions in nitric acid. Five-gram alloy samples were placed in about 75 ml. of acid; the other experimental conditions are given with each set of pictures. The explosions under acid were set off by dropping an electromagnetically controlled pointed steel rod onto the sample. The explosion in air (Figure 3) was set off by a spark from a Tesla coil. The latter sequence clearly demonstrates that the ignition is confined to the surface.

Figure 1

High Speed Photography of Explosion in Nitric Acid

Alloy Composition — 2% Zirconium

**Sample Preparation — 16 hours in 16M Nitric Acid at 25°C,
washed with water, dried with acetone.**

Photography — 5000 frames/second motion picture.

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Figure 2

A.

B.

C.

Standard Speed Photography of an Explosion of 20% Alloy

Alloy Composition — 20% Zirconium

Sample Preparation — 10 minutes in 8M nitric acid at 60°C

Photography — 64 frames/sec. motion picture

Initiation — Struck with steel rod

997-007

Figure 3

A. Shortly after sparking

B. $\frac{1}{100}$ second after A

High Speed Photography of Explosion in Air

Alloy Composition — 2% Zirconium

Sample Preparation — 30 minutes in 8M nitric acid
at 100°C, washed with water,
dried with acetone.

Photography — 3000 frames/second motion picture.

Initiation — Spark from Tesla coil.

997-008

Alloy composition and thermal history appear to have the most pronounced effect on the severity of the explosion. Alloys containing small percentages of zirconium require prolonged acid treatment to produce an explosion, but an alloy containing 20 w/o zirconium is a severe hazard after only several minutes in nitric acid. Particularly hazardous are those alloys which have been annealed or worked at 500°C and below. Samples of 2 w/o alloy which are quenched from the gamma region cannot be exploded in nitric acid, although there is evidence of the formation of a reactive surface coating. Samples of the partially dissolved gamma-quenched alloy which have been washed and dried glow momentarily when sparked with a Tesla coil. With alloys of higher zirconium content gamma-quenching may reduce the severity of explosion, although it is doubtful that the hazard of nitric acid etching or pickling can be eliminated by heat treatment.

B. Identification of Nitric Acid Residues

Low zirconium alloys may be contacted with nitric acid without incident provided no disturbance is permitted to occur. The coating which forms on the surface is black and explosive in the early stages of the dissolution, becomes gray on further treatment, and, eventually, on completion of the dissolution, becomes a completely passive residue. The residue contains uranium, but prolonged leaching with nitric acid fails to remove it. The X-ray diffraction powder pattern of the passive residue is neither that of urania nor zirconia but corresponds, as given in Table 1, to one of a series of solid solutions obtained in a study of the urania-zirconia phase equilibrium system by Lambertson and Mueller.⁽⁵⁾ The failure of nitric acid to leach urania from its solid solution in insoluble zirconia is readily understandable. Nitric acid also failed to leach the uranium from the urania-zirconia solid solutions prepared by fusion by Lambertson and Mueller.

Chemical analyses of three residues are presented in Table 2. X-ray diffraction showed that the nitrogen present in the residues was combined as zirconium nitride. This nitric acid-insoluble substance, present in low concentration in the original alloy, accumulated in the residue. Consequently, the atomic ratio of zirconium to uranium in these residues was based on the oxide content only.

It may be noted that in each dissolution the acid-soluble zirconium constitutes approximately 0.7 per cent by weight of the original alloy. Previously it had been observed that alloys containing from 0.14 to 0.7 w/o zirconium could be dissolved without residue in nitric acid.⁽⁶⁾ The amount of residue obtained from the nitric acid dissolution of gamma quenched 2 w/o alloy was about one fifth of that obtained from annealed or hot worked alloys. Therefore, it would appear probable that zirconium present in excess of the amount of solid solution in uranium is insoluble in nitric acid. The oxide residue is apparently formed by the oxidation of a phase in which excess zirconium is combined with uranium in an atom ratio of approximately three to one.

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Table 1

**COMPARISON OF X-RAY POWDER PATTERNS OF NITRIC ACID
RESIDUES AND A URANIA-ZIRCONIA SOLID SOLUTION**

Dissolution of 3.8% alloy, hot worked.

HNO ₃ Residue		(U,Zr)O ₂ ⁽⁶⁾ 76.7 mol % ZrO ₂	
d _A ^{0*}	I†	d _A ^{0*}	I†
3.35	35	3.33	15
3.02	100	3.00	100
--	0	2.63	45
2.64	55	2.59	55
--	0	1.98	30
1.84	65	1.84	80
--	0	1.76	?
1.62	20	1.58	50
1.60	55	1.56	75
1.52	15	1.50	40
--	0	1.315	30
1.32	10	1.30	40, broad
1.197	30	1.195	50
--	0	1.173	35
1.155	15	1.159	40
--	0	1.068	30
1.056	15	1.059	45
--	0	1.010	30
0.985	15	0.998	45
0.91	5, diffuse, broad	0.92	diffuse, broad
0.89	5, diffuse, broad	0.89	diffuse, broad
0.87	5, diffuse, broad	0.88	diffuse, broad
--	-, uncertain	0.87	diffuse, broad

*Interplanar spacing values in angstrom units.

†Line intensity: visual estimate based on scale of 100.

997-010

Table 2

CHEMICAL ANALYSES OF RESIDUES OBTAINED IN THE NITRIC
ACID DISSOLUTION OF URANIUM-ZIRCONIUM ALLOYS

Alloy Analysis, % by weight

	<u>Hot Rolled - 2.0 w/o Zr</u>	<u>Hot Rolled - 2.0 w/o Zr</u>	<u>Cast - 3.8 w/o Zr</u>
Zirconium	43.6	42.96 43.31 43.34	42.0
Uranium	35.7	36.30 35.55 35.70	36.4
Oxygen	20.1	21.9 22.4	--
Nitrogen	0.48	0.55	--
Atom Ratio: $Zr/(U + Zr)$	0.746	0.744	0.750
Gms. residue/100 g. alloy	3.08	2.80	7.37
Gms. Zr dissolved/100 g. alloy	0.66	0.79	0.70

Semi-quantitative calorimetric measurements were made of the heat of oxidation of some separated explosive coatings. The heats liberated indicated that 10 per cent or less of the coating material was metallic, the remainder being uranium-zirconium oxide. Dissolutions of hot worked 3.8 w/o alloy under a variety of conditions of acid concentration, time, and temperature were carried out in an attempt to find a set of conditions under which the rate of oxidation of the minor phase might be appreciably slower than its rate of exposure. This would permit the concentration of the inter-metallic constituent and its subsequent identification by X-ray powder diffraction methods. After the partially dissolved alloy samples were washed with water the coatings were scraped from the metal, washed with water and acetone, dried in vacuo, and loaded into Pyrex X-ray capillaries under an atmosphere of helium. Of the various powders obtained two gave an X-ray diffraction pattern (Table 3 and Figure 4A) which was unique and distinctly different from the patterns given by α -uranium, α -zirconium, or their oxides, carbides, nitrides, and hydrides, which presumably might be present. The strongest lines of the solid solution oxide were present at intensities indicating that it was the minor constituent. All other powders obtained, including a number which had been made by apparently identical chemical procedures, gave the characteristic pattern of the solid solution of the oxides in predominance, with only the strongest lines of the unique pattern in evidence.

Mueller, Chiswick, and Zegler of the Metallurgy Division of Argonne National Laboratory⁽⁷⁾ have obtained a diffraction pattern from a needle of 53 w/o (75 a/o) alloy which was homogenized by gamma annealing, quenched, cold worked at room temperature, and then annealed at 450°C. This pattern, which is also shown in Figure 4 and Table 3, is believed to be due to an inter-metallic phase (epsilon). The coincidences unequivocally establish the presence of the epsilon phase as a constituent of the explosive coatings from nitric acid dissolutions.

The superficial resemblance of the epsilon phase lattice to body-centered cubic* is not borne out by analysis of the $\sin^2\theta$ values, and it appears that the epsilon lattice is tetragonal.

*The interplanar spacings which have been asterisked in Table 3 coincide with spacings for the body-centered cubic gamma-quenched alloys.⁽⁷⁾ The evidence that these are accidental coincidences and are not indicative of the presence of retained gamma phase is as follows. (a) Gamma-quenched alloys have been annealed in the temperature range for disproportionation to γ -uranium and γ -zirconium. After this treatment no gamma lines were evident. Subsequent treatment below the gamma range produced the (B) pattern. (b) Hot worked alloys, in which the gamma phase can not be retained, were used to produce the material giving the (A) pattern.

Table 3

COMPARISON OF X-RAY PATTERNS FOR THE "EPSILON PHASE"

A: From powders obtained by nitric acid treatment of hot worked 3.8 w/o Zr alloy.

B: From U-Zr alloy needle, 53 w/o Zr, by physical treatment⁽⁸⁾

A			B		
d_A°	$\sin^2 \theta$	I	Component	d_B°	I
4.37	0.03113	50	ϵ	4.33	20
3.10	0.06184	45	ϵ	3.09	50
3.02		60	(U,Zr)O ₂		
2.52	0.0938	100	ϵ	*2.52	100
--	--	0	--	2.18	10
1.953	0.1558	60	ϵ	1.951	80
1.83-1.86		20	(U,Zr)O ₂		
1.780	0.1876	60	ϵ	*1.780	80
--	--	0	ϵ	1.645	20
1.6		faint band	(U,Zr)O ₂		
1.549	0.2478	20	ϵ	1.548	40
1.453	0.2815	60	ϵ	*1.452	90
1.317	0.3426	60	ϵ	1.319	70
1.258	0.3755	50	ϵ	*1.257	60
--	--	0	ϵ	1.207	20
1.16	0.437	20	ϵ	1.166	40
1.125	0.4696	45	ϵ	*1.125	50
1.06	0.5306	40	ϵ	1.061	60
1.03		5	ϵ	*1.028	30
1.00		5	ϵ	1.006	30
0.98		20	ϵ	0.978	40
0.95		50	ϵ	*0.952	70
--	--	0	ϵ	0.935	30
0.91		5	ϵ	0.910	40
0.87		5	ϵ	0.876	40
0.84		20	ϵ	*0.839	50
0.81		20	ϵ	0.811	60
--	--	--	ϵ	0.797	40

d_A° : interplanar spacing values in angstrom units.

$\sin^2 \theta$: square of sine of the Bragg angle θ with Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$

I: visual estimate of line intensity based on a scale of 100. The line absences in A are accounted for by the presence of oxide which diluted the other component so that its weak lines were undetected. The needle specimen (B) gave spotty diffraction arcs and reliable intensity estimations were difficult to make.

*See Footnote, page 12.

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FIGURE 4

X-RAY POWDER PATTERNS OF THE EPSILON PHASE

- A. RESIDUE FROM NITRIC ACID DISSOLUTION
OF HOT-WORKED 3.8w/o ALLOY.
- B. COLD-WORK NEEDLE OF 53w/o ALLOY.

Courtesy of Chiswick, Mueller, & Ziegler

C. Dissolution in Hydrogen Chloride - Ethyl Acetate

A search was made for a reagent which would preferentially attack the matrix and leave the minor phase as a residue. An ethyl acetate solution of hydrogen chloride was found to have this property, dissolving the matrix rapidly and giving as principal reaction products uranium tetrachloride, hydrogen, and a finely divided black powder. Various alloys were dissolved by this method. The black, finely divided residues were separated mechanically from excess metal, washed repeatedly with fresh ethyl acetate, and dried in vacuo. These powders were extremely pyrophoric. The powders react rapidly with 0.1 M hydrofluoric acid producing copious amounts of hydrogen and leaving a precipitate of uranium tetrafluoride. The hydrogen evolved during several of these dissolutions was collected and measured volumetrically; chemical analyses were made on the precipitate and hydrofluoric acid solution. The results are given in Table 4. Samples of the residue from the annealed alloys were transferred both as suspension in ethyl acetate and as dry powders under an atmosphere of helium to Pyrex X-ray capillaries. The X-ray powder diagram obtained was unique and distinctly different from that of the solid solution oxide (Table 1) and from the patterns given by α -uranium, α -zirconium, or their oxides, carbides, nitrides, and hydrides which presumably might be present. It is also unlike the epsilon phase pattern (Table 3). The interplanar spacings calculated are given in Table 5. The differences in lattice spacings may be connected with differences in previous thermal history of the alloy.

Table 4

CHEMICAL ANALYSES OF HYDROGEN CHLORIDE - ETHYL ACETATE RESIDUES

<u>Alloy, % Zr</u>	<u>Treatment</u>	<u>Uranium, % by wt</u>	<u>Zirconium, % by wt</u>	<u>ml Hydrogen per mg sample (S.T.P.)</u>
3.8	Hot Worked	46.1, 43.8	--	0.360
2.0	Annealed, 500°C, 7 days	--	53.2	0.358
3.8	Annealed, 500°C, 7 days	--	53.2	0.334
	(Calc. 25 mole % U, 75 mole % Zr)	46.5	53.5	0.351

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Table 5

LATTICE SPACINGS EXHIBITED BY X-RAY POWDER PATTERNS FROM
DISSOLUTIONS OF ALLOY IN HYDROGEN CHLORIDE - ETHYLACETATE

Dissolution of 3.8 w/o alloy, 500°C annealed.

d_A°	Intensity (scale of 100)	Line Characteristics
4.56 $\pm$ 0.01	20	
3.16 $\pm$ 0.01	40	
2.85 $\pm$ 0.01	100	
2.54 $\pm$ 0.01	55	
2.33 $\pm$ 0.01	25	Diffuse
1.97	25	Very diffuse band
1.93		
1.790 $\pm$ 0.005	30	
1.720 $\pm$ 0.005	40	
1.65	10	
1.515 $\pm$ 0.002	40	
1.422 $\pm$ 0.002	35	
1.16	10	
1.12	10	Diffuse, uncertain
1.06	?	Uncertain
1.02	?	Uncertain
0.98	?	Uncertain

D. Discussion

The phase diagram of the uranium-zirconium system, recently compiled by Saller⁽⁸⁾ from various sources, is shown in Figure 5. Although some of the features are still in controversy this diagram represents the presently-held opinion of investigators at several laboratories. The salient points of interest are as follows:

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FIGURE 5. URANIUM-ZIRCONIUM CONSTITUTIONAL DIAGRAM

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1. An intermetallic compound, UZr_3 , exists in which α -uranium and α -zirconium have limited solid solubility. This solid solution is designated as the epsilon phase and has approximately lower and upper limits of 68 a/o (41 w/o) and 75 a/o (53 w/o) zirconium. This phase may exist in more than one modification.

2. Zirconium is soluble in α -uranium to the extent of about 0.6 w/o at "room temperature," and to about 2 w/o at 700°C.

The observations made in the course of this research tend strongly to support the above statements.

1. A reasonably pure metallic substance has been obtained as a residue of the dissolution of annealed alloys in hydrogen chloride-ethyl acetate. This residue exhibits a unique diffraction pattern which originates from a component of the alloy system which is neither α -uranium nor α -zirconium. It is almost certainly due to one of the epsilon phases. It is somewhat surprising that the analyses agree much more closely with the supposed upper existence limit of composition than with the lower one. This would indicate that the solubility of uranium in epsilon is less than is shown by the phase diagram.

A metallic substance present in the explosive coating arising from nitric acid dissolutions of alloys also has been shown to be due to one of the epsilon phases. Oxidation of this phase results in a solid solution of the dioxides of uranium and zirconium in a mole ratio of one to three. This also indicates a more restricted solubility of uranium in epsilon.

2. The fact that 2 w/o alloys quenched from the gamma region could not be exploded in nitric acid and leave little residue after dissolution indicates that supersaturation of α -uranium with zirconium occurs readily on quenching. Annealing at elevated temperatures or working increases the explosibility and the amount of nitric acid residue. Apparently the epsilon phase crystallizes during these treatments. The solubility in nitric acid of zirconium to the extent of 0.7 per cent by weight of the annealed alloys is expected if the alpha solid solution is completely soluble in nitric acid.

Recent X-ray diffraction studies in the Metallurgy Division of Argonne National Laboratory have shown that the epsilon phase probably disproportionates at about 600°C to α -uranium and α -zirconium.⁽⁹⁾ X-ray diffraction studies by Petersen of the Ames Laboratory⁽¹⁰⁾ have shown α -zirconium to be present in explosive residues from the nitric acid dissolution of alloys annealed at 600°C. It would therefore appear that the explosive constituent may be either epsilon or α -zirconium depending on prior thermal history.

997-018

With regard to the explosibility of zirconium-uranium alloys it is not proposed that the epsilon phase or α -zirconium is intrinsically explosive. Finely divided metal powders, except for those of the most noble metals, can react explosively with oxygen or nitric acid. In the present case the state of great dispersion of the minor phase in the alloys and the slow attack by nitric acid on the dispersed material permit the accumulation of a typical explosive powder on the surface of nitric acid-treated specimens.

V. PREVENTIVE MEASURES

The addition of fluoride in sufficient quantity to the nitric acid bath eliminates the explosion hazard in pickling, etching, and dissolution of the uranium-zirconium alloys. The nitric acid-fluoride medium dissolves the uranium-zirconium intermetallic phase as rapidly as it is exposed by dissolution of the uranium matrix. Alloys containing 2, 4, 10, and 20 w/o zirconium have been safely and completely dissolved in this medium. Throughout dissolution in this medium each sample of alloy remained shiny, and no trace of an explosive surface coating was detected.

A series of photomicrographs, Figure 6, shows the difference between the action of nitric acid and that of nitric-hydrofluoric acid on samples of 2 w/o alloy. In Figure 6B, the original cutting marks are still visible in the surface coating although 10 per cent of the uranium has been dissolved. The irregular black spots are holes formed in the surface coating by the escape of gas during dissolution. The addition of a small quantity of fluoride to the nitric acid bath gave a lustrous, crystalline surface as shown in Figure 6D. The black spots are holes in the bulk metal and result from an uneven attack by the acid.

By varying the quantity of fluoride present during the nitric acid dissolution of low zirconium alloys it has been observed that a mole ratio of fluoride to zirconium of four is the minimum required to prevent the formation of a surface coating. This is approximately one gram of fluoride per gram of zirconium. A molar ratio of fluoride to zirconium of four had been previously demonstrated to be required for the complete dissolution of zirconium metal in hydrofluoric acid.⁽¹¹⁾

Alloys containing 2, 4, 10, and 20 w/o zirconium have been satisfactorily pickled in a solution 12 M in nitric acid and 1.0 M in fluoride at 50 to 75°C. Fluoride should be added to this solution from time to time because of its depletion by the pickling process. When large pieces of alloy are to be pickled a reasonable precaution is the preliminary testing of a small sample of the same material to insure the safety of the larger operation. Uranium tetrafluoride may form on the surface of the specimen as a result of pickling in this solution. It may be removed by immersion in hot 0.5 M aluminum nitrate.

997-019

Figure 6

Photomicrographs of Uranium-Zirconium Alloy Before
and After Acid Treatment.

Alloy Composition — 2% Zirconium

Magnification — 40 Diameters

A. Untreated Alloy

B. After 25 minutes in 8M HNO_3
at 100°C .

C. After 25 minutes in 8M HNO_3
at 100°C . Note the scraped
surface coating.

D. After 25 minutes in 8M HNO_3 ,
0.02M HF at 100°C .

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Detection and safe removal of a potentially explosive coating are more difficult operations than prevention of its formation. Visual inspection is probably the best means of detection, but handling of the specimen should be kept to a minimum. An alloy specimen which remains coated for any length of time is potentially dangerous. A test which has been applied to suspected samples consists of sparking or striking the specimen after it has been thoroughly washed with water and acetone and then dried. With potentially hazardous materials this often results in spectacular burning, but, unfortunately, failure to burn in this test does not assure a surface free of explosive material. In several instances samples which failed to burn when this test was applied exploded violently when placed in a nitric acid bath.

It is imperative that adequate safety equipment (face shields and protective clothing!) should be used for all operations involving the dissolution, pickling, or etching of zirconium-uranium alloys. If an explosive surface is suspected the specimen should be flooded with water. Dilute hydrofluoric acid may then be added. These steps must be performed cautiously and without disturbance of the specimen. It has been reported that explosions may occur even after submergence of the active sample in water or after fluoride has been added to the acid bath containing the active sample.⁽⁴⁾ These explosions were probably caused by disturbance of the coating, which contained both the active constituent and occluded nitric acid.

The use of other chemical media, particularly non-oxidizing acids, for the pickling, etching, and dissolution of low zirconium alloys may be as hazardous as the use of nitric acid. If the uranium matrix is dissolved and the more slowly soluble minor phase is allowed to accumulate as a finely divided metal powder, subsequent exposure of the residue to an oxidizing agent or air may result in an explosion even more violent than that encountered using nitric acid.

A sound motion picture entitled "Explosions of Uranium - Zirconium Alloys in Nitric Acid," Argonne National Laboratory Motion Picture 108-512, is available to interested laboratories. The film contains both standard and high speed shots of explosions in nitric acid and air and a complete discussion of the use of fluoride to prevent the explosions.

997-021

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