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ISOTOPES DEVELOPMENT CENTER

PROGRESS REPORT

CURIUM PROGRAM

NOVEMBER 1962

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ORNL-TM-452

Contract No. W-7405-eng-26

ISOTOPES DEVELOPMENT CENTER

PROGRESS REPORT

CURIUM PROGRAM

November 1962

Eugene Lamb, Isotopes Division

Prepared From Reports by:

F. T. Binford, Operations Division
T. A. Butler, Isotopes Division
D. E. Ferguson, Chemical Technology Division
R. A. Robinson, Isotopes Division
R. W. Schaich, Isotopes Division

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CURIUM PROGRAM

Eugene Lamb

ABSTRACT

A progress report of ORNL activities in the development of production capacity of Cm^{242} and Cm^{244} for isotopic power programs is given. This report covers development of irradiation capsule designs and reactor capacity, chemical separation of the Cm^{242}, and fabrication of the Cm^{242} heat source.

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1.0. IRRADIATION OF Am^{241}

1.1. Am^{241} Irradiation Schedules

A tentative (Am^{241}) irradiation schedule has been determined based on the Cm^{242} production requirements in FY 1964 and is tabulated in Table 1.1.1. Sufficient Cm^{242} will be produced for the SNAP-13 source (~2.25 g) and the prototype SNAP-11 source (8 g). Two additional ORR irradiations may be scheduled during FY 1964.

Table 1.1.1. Am^{241} Irradiation Schedule

Irradiation Unit	Am^{241} (g)	Reactor	Entry Date	Removal Date
Martin Co.	12	MTR	7-15-63	9-15-63
ORNL	30	ORR	8-30-63	11-18-63

1.2. Irradiation Target Fabrication

Four standard-size Gd_2O_3-Al pellets were fabricated with a water-soluble dye intermixed with powder matrix. These pellets were subjected to a boiling water test for 96 hr with no indication of leakage from the pellet. Thirteen additional pellets were fabricated with 1-1/4-in. aluminum sleeves, which eliminate the need for vibration compaction and reduce the outside surface contamination. The results were satisfactory and the wall thickness of the pellet was increased.

The particle size of powdered Am_2O_3 prepared at Rocky Flats, Colorado, was measured and the results are tabulated in Table 1.2.1.

Table 1.2.1. Am^{241} Particle Size

Screen Size	Micron Size	Percent
40	350	9.29
50	295	9.29
60	250	7.16
70	211	3.78
80	177	3.10
100	150	5.30
<100	<150	61.9

Five 1/2-in. OD by 8-in. aluminum capsules were remotely welded using three pre-heat passes and then two welding passes at 16-17 amp with

a rotation speed of 2 RPM. Four capsules were approved after visual examination; the fifth capsule required an additional cycle to eliminate a few pin holes. Further welding studies will be made to determine the optimum conditions.

Experiments were conducted on a hydrostatic swaging technique to collapse the walls of the aluminum capsules around the americium pellets. Two 3/8-in. capsules were used, each having a clearance of 0.15 in. between an aluminum rod and the inside wall of the capsule. A hydrostatic pressure collapsing device was attached to a Blackhawk 50-ton press and the cylinders were collapsed at 8000 and 9000 psig respectively. Both capsules were leak tested with ethylene glycol under approximately 20-in. H_2O vacuum, and diameter measurements were made at various points along the length of the capsules. In both cases the diameter varied from 0.360 in. to 0.361 in. except for a 1/8-in.-wide ridge which was most prominent at the center and gradually tapered toward the ends of the capsules.

The capsules were then cross-sectioned and etched in a caustic solution. Examination under magnification revealed the annular space between the rod and the jacket was within the specified 0.001-in. clearance except in the area around the ridge. The clearance in this region was 0.010 to 0.012 in. at the center of the ridge with a gradual tapering to <0.001-in. clearance.

Further experiments were run on 1/2-in. OD capsules with steel rods inserted to provide 0.007-in. clearance. The collapsing pressure used on each tube was 6000, 8000, and 9300 psig, respectively. Each capsule passed the leak test, and very little difference was noted in the diameter measurements on the tubes swaged at 8000 and 9300 psig. The tube swaged at 6000 psig was approximately 0.001 in. larger in OD. A slight ridge was noted on all three tubes but in each case amounted to <0.003 in. Cross sections of the tubes were etched in a caustic solution and examined under magnification. The 8000-psig cross section was within the 0.001-in. clearance, and the 6000-psig cross section contained one small area under the ridge where the clearance varied between 0.001 and 0.003 in.

Calculations were made to determine the minimum free space required in the 1/2-in. capsules for gas expansion during reactor irradiation. The calculations were based on the assumptions that 50% of the americium would be converted to curium and that all the oxygen and helium released would remain in the free state. The maximum allowable pressure for the capsule is 605 psi based on the yield strength and 1330 psi based on the ultimate strength. Using an ID of 0.42 in. after swaging, the length of free space necessary for gas expansion is 1.165 in. based on the yield strength.

The design and fabrication status of the target preparation equipment is shown in Table 1.2.2.

Table 1.2.2

Equipment	Design % Complete	Fabrication % Complete
Blender	100	0
Pellet press	100	100
Capsule loading device	100	100
Welder modifications	95	90
Ultrasonic cleaner	100	50
Hydraulic swager	100	10
Leak testing equipment	90	0
Pellet punches	100	Ordered
Pellet dies	100	Ordered
Capsule tubing	100	Ordered
Swaging pump	100	Ordered

1.3. Target Shipping Casks

Bureau of Explosives Permit No. 1495 has been assigned to the unirradiated target shipping cask.

As indicated in the previous monthly report, the MND cask has adequate neutron shielding but insufficient gamma shielding. A study of the possibility of adding lead shielding to the outside of the cask has been initiated. Design of a new insert for the MND cask will be completed this fiscal year.

2.0. CHEMICAL PROCESSING OF Cm^{242}

Work was continued on the adaptation of the Tramex Process to the recovery of Cm^{242} from irradiated Am^{241} targets and on the design and construction of the Curium Recovery Facility.

2.1. Chemical Process Development

Tramex Feed Adjustment Studies. A number of simulated feeds containing no free acid, 0.2 M $AlCl_3$, and from 6 to 10.5 M LiCl were prepared to determine the maximum LiCl concentration that can be obtained by distillation without causing aluminum precipitation because of acid deficiency. The starting solutions contained $AlCl_3$ and LiCl in the proper ratio and 2 M HCl. Evaporation distilled off excess acid and concentrated the solutions. All adjusted feeds containing 0.2 M $AlCl_3$ and up to 10 M LiCl (boiling point 128°C) were stable with no evidence of aluminum precipitation after cooling

to room temperature. A small amount of aluminum precipitated from feed adjusted to 0.2 M $AlCl_3$ and 10.5 M LiCl (boiling point 131.5°C). These results indicate that satisfactory Tramex feed can probably be obtained by simple distillation. However, this must be confirmed in full scale testing in plant equipment.

Tramex Flowsheet Test Using Cm^{242}. The possible extraction of cerium was noted last month. Further study of the analytical results has shown that the activity observed was indeed Ce^{141}, but that the cerium probably entered the pregnant organic stream by entrainment rather than by extraction. This is supported by the fact that the ratio of cerium to curium in the pregnant organic, while initially quite high, decreased continually in successive samples until it was less than one-tenth the value in initial samples.

Evaluation of Triisooctyl Amine as Tramex Extractant. The use of triisooctyl amine (TIOA) as extractant for the Tramex process has been re-evaluated since it is now commercially available from Archer Daniels Midland Company, Minneapolis, Minnesota. Although TIOA has slightly better extraction properties than Alamine 336, this advantage is offset by its greater viscosity which results in slower phase separation. Curium distribution coefficients from 10 M LiCl-0.2 M $AlCl_3$ and viscosities for various solvents were as follows:

Solvent	K_d of Cm	Viscosity, centipoise
0.6 M Alamine 336·HCl in diethylbenzene	6.6	4.95
0.6 M TIOA·HCl in diethylbenzene	8.2	5.83
0.6 M TIOA·HCl in diisopropylbenzene	10.6	7.80

Since there appears to be no great advantage in using TIOA, Alamine 336·HCl diluted in diethylbenzene is still the recommended solvent for the Tramex process.

Physical Properties of Tramex Solutions. A program was started to determine physical properties of LiCl and mixed LiCl-$AlCl_3$ solutions. Densities, refractive indices, boiling points, and viscosities have been determined for LiCl solutions from 6 to 11 M and for 9, 10, and 11 M LiCl solutions containing $AlCl_3$ up to the point of solubility. These studies are continuing.

Effect of High-level Alpha Activity on Ion Exchange. By pressurizing a column of -270 mesh cation exchange resin, the effects of gassing normally associated with high alpha activity solutions were controlled well enough to give satisfactory separation of americium and curium by chromatographic elution with ammonium alpha hydroxyisobutyrate. The product cut contained 96% of the curium free of americium.

[redacted]

2.2. Curium Recovery Facility

The design of Cell 4 is 95% complete. The sample removal cubicle and carrier design were revised to allow the transfer of four high-activity sample bottles instead of one at a time to the analytical labs. This was precipitated by a re-evaluation of the method of sampling and the number of required samples. Dilutions originally planned to be performed in the cell become too burdensome during production runs, and most samples will be transferred without dilution.

The first batch of Cm^{244} solution from Cell 1 was transferred into the under-floor storage tank without difficulty, and the cell was entered immediately afterward. There is no detectable increase in cell background radiation.

Cell 3 has been diverted to a support cell for the processing in Cell 4. It will be prepared to accommodate chemical glassware on a table or installed on prefabricated racks through the roof hatch. This cell will be used for the separation of americium and curium.

Construction on the facility is proceeding as planned. Due to delays in procurement, however, completion of the facility is not expected until April 1, 1963.

3.0. Cm^{242} SOURCE FABRICATION

3.1. Chemical Process Development

Oxalate precipitations may be desirable for the separation of curium from many contaminating metal ions. Studies are described below on come of the ions thought to be possible contaminants. Cerium was used as a substitute for curium to determine the quantity of contaminating ions carried in the oxalate precipitate.

Nickel Decontamination. Table 3.1.1 shows the data obtained by attempting to separate nickel from 500 ml of a 2.5×10^{-3} M $Ce(NO_3)_3$ solution by oxalate precipitation with the use of Ni^{65} and Ce^{144} tracers. Oxalic acid was added to a solution containing $Ni(NO_3)_2$, $Ce(NO_3)_3$, 1 M HNO_3; then the pH was adjusted to 2-5 with NaOH.

Table 3.1.1. Decontamination of Cerium from Nickel by Oxalate Precipitation

Ni(II) (mole/ liter)	Oxalate (mole/ liter)	Percent Cerium in Precipitate	Percent Cerium in Solution	Percent Nickel in Precipitate	Percent Nickel in Solution	Decontamination Factor
0.0031	0.01	98.5	1.5	trace	98+	$\sim 10^2$
0.0061	0.01	95.8	4.2	trace	99+	$>10^2$
0.0092	0.01	90.4	9.6	trace	99+	$>10^2$

[redacted]

[redacted]

Table 3.1.1 (continued)

Ni(II) (mole/ liter)	Oxalate (mole/ liter)	Percent cerium in Precipitate	Percent cerium in Solution	Percent Nickel in Precipitate	Percent Nickel in Solution	Decontamination Factor
0.012	0.01	97.1	2.9	trace	99+	~10^3
0.017	0.01	95.8	4.2	0.5	99.5	~200
0.102	0.15	95.2	4.8	58	42	1.7
0.17	0.15	97.9	2.1	78	22	1.3
0.24	0.15	99.1	0.9	99.4	0.6	1.0

These data clearly indicate that 1 g/liter of nickel can be separated readily by the oxalate precipitation.

In another experiment, it was found that 90-95% of the nickel in concentrations up to 20 g/liter could be kept in solution by maintaining an oxalate concentration in excess of 3 moles of oxalate to 1 mole of nickel. When the oxalate to nickel molar ratio was slightly greater than 1:1, only about 5% of the nickel remained in solution.

Zirconium Decontamination. To 500 ml of 1 M HNO_3 was added 0.3 or 0.5 g of $ZrOCl_2$, 0.5 g of $Ce(NO_3)_3$, ~1 mc of Zr^{95}-Nb^{95} tracer, and 0.1 mole of $H_2C_2O_4$. Adjustment of the pH with NaOH yielded a precipitate of $Ce_2(C_2O_4)_3$ which was filtered and rinsed with a dilute oxalic acid solution. A sample of the filtrate was counted and the precipitate was redissolved in 100 ml of 5 M HNO_3 containing a trace of $KMnO_4$. After dissolving the precipitate, the solution was diluted to 500 ml with water and a sample was withdrawn and counted. The precipitation and sampling were then repeated on the redissolved $Ce_2(C_2O_4)_3$. The zirconium was separated from cerium by factors of about 50 and 10^3 by one and two precipitations, respectively, as shown on Table 3.1.2.

Table 3.1.2. Decontamination of Cerium from Zirconium by Oxalate Precipitation

Zr(IV) (mole/liter)	No. of Precipitation	Percent Zirconium in Precipitate	Percent Zirconium in Solution	Decontamination Factor
3.4×10^{-3}	1	1.2	98.8	80
	2	trace	100	~10^2
Total decontamination factor, two precipitations				>10^3
3.4×10^{-3}	1	1.1	98.9	90
	2	trace	100	~10^2
Total decontamination factor, two precipitations				>10^3
5.6×10^{-3}	1	3.1	96.9	30
	2	3.9	96.9	25
Total decontamination factor, two precipitations				~10^3

[redacted]

Table 3.1.2 (continued)

Zr(IV) (mole/liter)	No. of Precipitation	Percent Zirconium in Precipitate	Percent Zirconium in Solution	Decontamination Factor
5.6×10^{-3}	1	9.1	90.9	10
	2	1.3	98.7	75
Total decontamination factor, two precipitations				$\sim 10^3$

A 5.6×10^{-3} M zirconium solution containing Zr^{95} tracer was evaporated to dryness before the first precipitation in order to convert the zirconium to an insoluble form. The data indicate that the precipitation was only slightly less effective under these conditions than it was when zirconium was present in soluble form. Hence, it may be concluded that high decontamination from zirconium is feasible by oxalate precipitations.

Americium Chemisty. A previous report has shown that Am(III) can be oxidized to Am(VI) with cold $NaBiO_3$, which has an advantage over persulfate in that bismuthate does not form peroxide by an undesirable side reaction as in the case of persulfate. Thus, control of acidity is not critical and the bismuthate method may be more reliable for analytical purposes. In addition, it is known that peroxide can coexist with persulfate. If bismuthate can be shown to react with peroxide, it can be considered as a holding oxidant, and hence more reliable than persulfate as an oxidizing agent for americium.

Since $NaBiO_3$ is a solid, good agitation is essential in order to oxidize americium in solution. Table 3.1.3 shows that intermittent agitation by hand shaking is not sufficient. Table 3.1.4 shows that magnetic stirring considerably decreases the amount of time required to oxidize americium.

Table 3.1.5 shows that LaF will not carry either Am(III) or Cm(III) at high acidities or at low concentrations of fluoride. However, this difficulty can be easily avoided by decreasing the acid concentration and by increasing the fluoride ion concentration.

Table 3.1.3. Time Effect for Oxidation of Americium by Sodium Bismuthate with Intermittent Agitation*

Oxidation Time (hr)	Percent Oxidized
0.5	71
1.5	87
2	91
3	94
4	94

*Samples hand shaken every 5 min; oxidation in 8 N HNO_3.

Table 3.1.4. Time Effect for Oxidation of Americium by Sodium Bismuthate When Samples are Stirred*

Oxidation Time (min)	Supernate (counts/min)	Precipitate (counts/min)	Percent Oxidized
15	12,500	10,800	54
30	12,700	6,600	66
45	17,800	2,100	90
60	21,900	600	98

*Oxidation carried out in 8 N HNO_3 with magnetic stirring

Table 3.1.5. Effect of Acidity on the Carrying of Americium(III) by Lanthanum Fluoride

HNO_3 Present		Concentrated	NH_4F Used		Percent	Percent
Volume (ml)	Concentration	NH_4OH Added (ml)	Volume (ml)	Concentration	Am(III) Carried	Curium Carried
8	6 N	-	2	1 M	99.9	99.8
8	8 N	-	2	1 M	14	7
8	8 N	-	3	3 M	57	62
8	8 N	2	3	3 M	100	-

3.2. Source Fabrication Development

Gadolinium-Rhodium Cermets. A three to one volume ratio of rhodium to gadolinium was used to fabricate a full-scale cermet to simulate a SNAP-13 pellet. The pellet was pressed in a 2.1-cm-diam die at 29,000 psi. The green pellet was sintered 4 hr at 1725°C, and an excellent cermet was produced as shown in Fig. 3.2.1. Table 3.2.1 gives the dimensions of the green and sintered pellet.

Table 3.2.1. Pellet Dimensions

Measurement	Green Pellet	Sintered Pellet	Shrinkage (%)
Diameter (cm)	2.10	1.85	12
Height (cm)	0.80	0.73	9

An investigation of the rhodium and Gd_2O_3 powder particle size is under way to determine the optimum conditions for cermet formation. The Gd_2O_3

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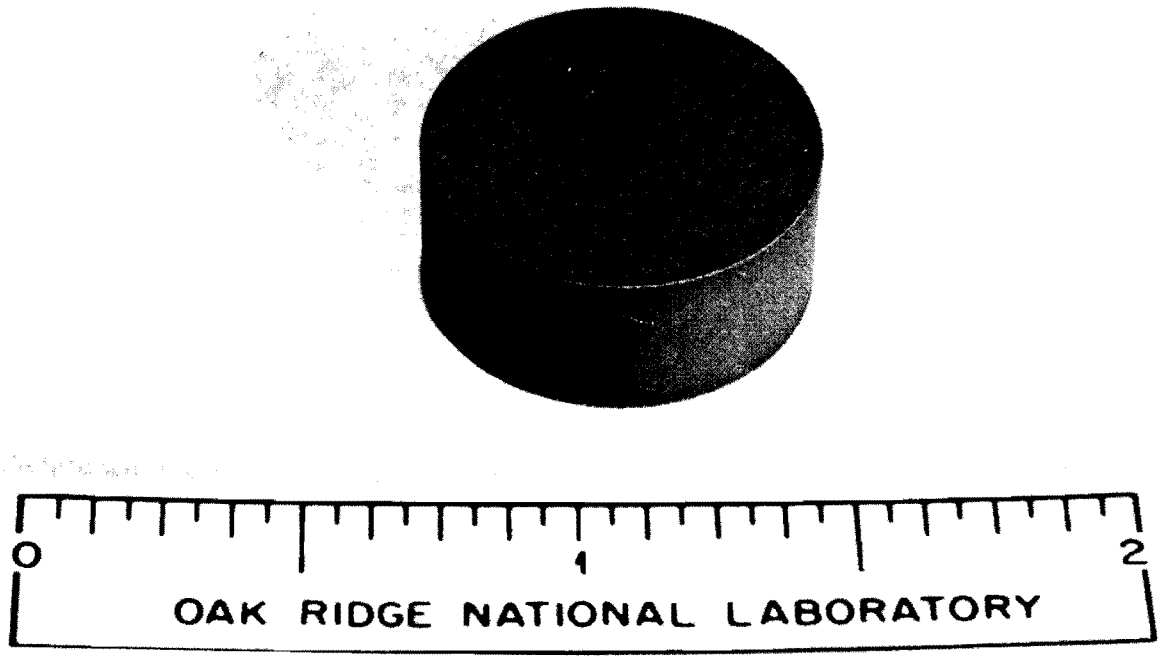

Fig. 3.2.1. Gd_2O_3-Rh Cermet

[redacted]

particle size was determined to be < 200 mesh while the rhodium particle size varied as shown in Table 3.2.2.

Table 3.2.2. Rhodium Powder Particle Size

Screen Size Mesh	Percent
>100	11
100 to 200	12
200 to 230	5
<230	72

Since rhodium powder will be the controllable factor as to particle size, investigations to form a rhodium powder of <200 mesh will continue, and the effects of particle size on cermet formation will be studied.

The effect of metal contaminants on the cermet is under investigation, and three pellets were formed using 1% of Fe, Ni, and Cr as impurities. The addition of Fe_2O_3 resulted in a cermet with a small quantity of Fe_2O_3 flowing out of the cermet. The addition of chromium showed no visible effects while the nickel-contaminated pellet resulted in a slightly deformed pellet with a NiO coating on the alundum tray. Further tests will be performed on these pellets, which are shown in Fig. 3.2.2.

3.3. Source Fabrication Facility

The CPFF contractor initiated the GPP modifications on Building 3028 on November 12, 1962. The estimated completion date for this phase of the project is April 1, 1963.

The design status for the Source Fabrication Facility is listed in the following table:

Item	Percent Complete
Cell cubicles	60
Pm^{147} cell alterations	99
Waste disposal system	15
Feed transfer station	2
Cell equipment	2
Manipulator decontamination station	0
Cubicle access enclosure	0

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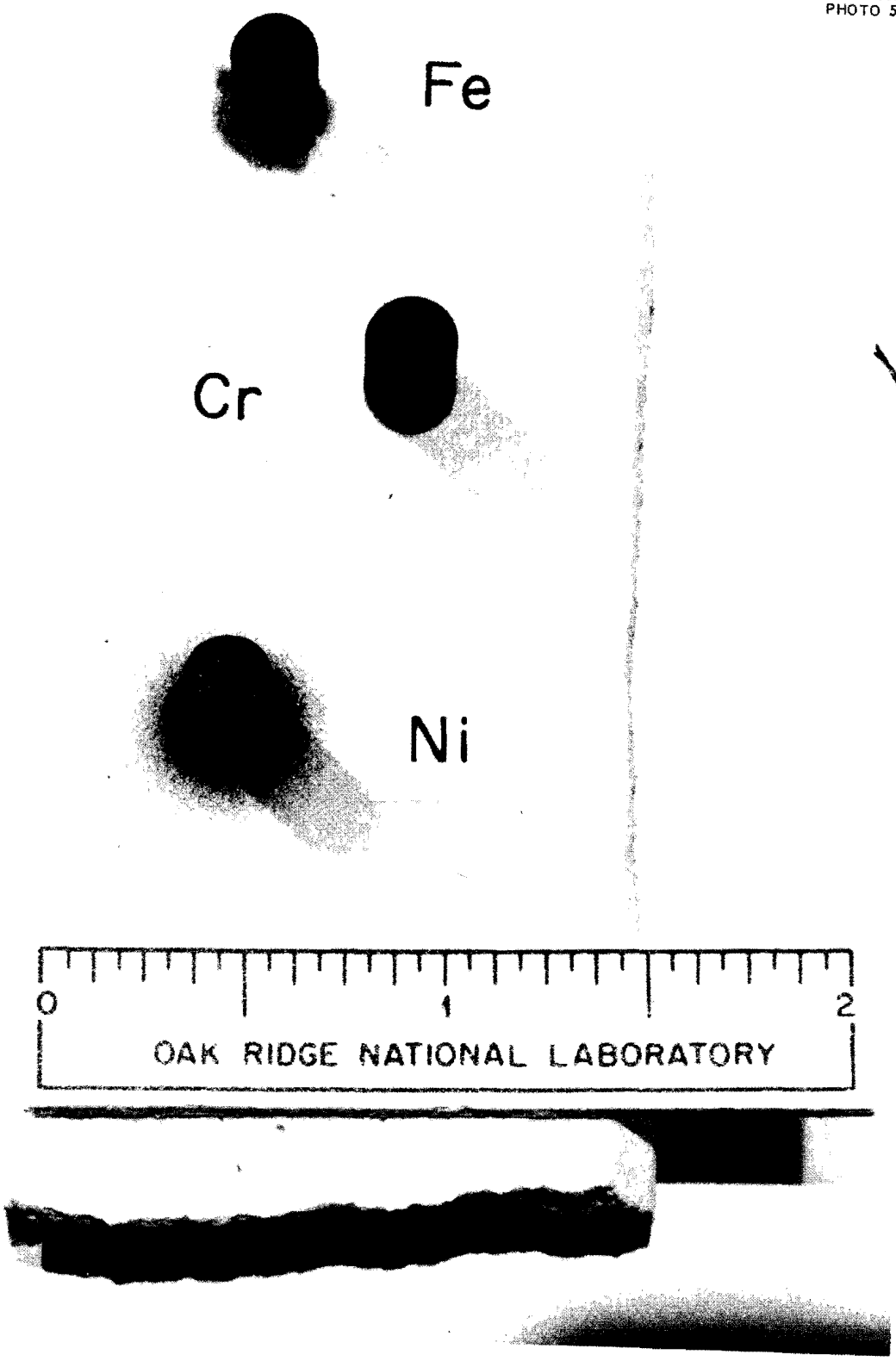

Fig. 3.2.2. Metal-Contaminated Cermets

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