1
METALLURGY AND CERAMICS

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QUARTERLY SUMMARY RESEARCH REPORT

For July, August, and September 1951

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by

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QUARTERLY SUMMARY RESEARCH REPORT

For the period July, August and September 1951

This report is prepared from material
submitted by the group leaders of
the Laboratory.

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METALLURGY

8

Under the direction of F. H. Spedding, H. A. Wilhelm
B. A. Rogers, O. N. Carlson, P. Chiotti
and D. Peterson

1. Zirconium

1.1 Ore Treatment

The reaction between molten caustic soda and zircon sand at 550°C is proving to be a very successful method of opening this ore. The product from this pseudo-fusion consists mainly of sodium silicate and sodium zirconate. The silicate is water soluble and can largely be removed by a simple wash treatment. A washing study was conducted and it was concluded that above a certain amount of wash very little additional influence on the quality of the product was obtainable. Roughly one gallon of water per pound of reaction product was considered an adequate wash.

One of the difficulties encountered in this process is the relatively high silicon content of the product. This is assumed to be due to the presence of small amounts of a water insoluble double salt (sodium zirconium silicate) formed during the high temperature reaction. Solution of the washed sodium zirconate with hydrochloric acid makes possible the simple oxychloride crystallization. In addition to general purification, it has been found that the silicon content can be reduced to less than 0.1% by this crystallization.

The above caustic treatment process is being tested as a pilot plant operation in this Laboratory. At present, 75 pounds of zircon ore are treated at one time in an iron pot with 100 pounds of commercial grade 76% Na₂O flake caustic. The pot with the charge is heated by lowering it into a pit-type gas-fired furnace set at 650°C. During the heating the caustic fuses and there is no evidence of action between it and the sand until the charge reaches about 550°C. Here rather turbulent action takes place with the formation of the solid granular product which represents better than 99 per cent yield of the sodium salts of zirconium and silicon from the zircon sand. This product is washed in a 500 gallon agitation tank and then dried on a centrifuge. Acid solution of the sodium zirconate and crystallization are made in steam-jacketed, glass-lined vessels. The

zirconyl chloride is freed of mother liquor, dried and washed on a centrifuge. A concentrated water solution of the chloride is prepared and then clarified on a filter press. The solution is then ready for making feed for the liquid-liquid extraction process.

It has been estimated that, on a commercial-scale operation, the chemical costs involved would be less than 30¢ per lb. of zirconium available in solution, or less than 10¢ per lb. of zirconyl chloride produced. Although not complete, this figure compares favorably with the price of zirconium produced as the commercial tetrachloride and has perhaps greater purity than the tetrachloride. It should be pointed out that the zircon sand is used as it comes from the ore concentration process, and that the product of the reaction is a soft granular material. Therefore no costly grinding operations are necessary in connection with this process. An aqueous sodium silicate solution obtained by a wash treatment of the granular product might possibly have some value commercially as such. Silica gel can readily be prepared from this wash solution by the addition of acid. The washed sodium zirconate can be employed to produce other commercially important zirconium, or zirconyl, salts such as sulfate or nitrate by simple treatments employing sulfuric or nitric acid. Plans are being made to test the above molten caustic treatment on other zirconium bearing ores especially those containing higher percentages of zirconium oxide than zircon.

1.2 Liquid-Liquid Extraction

It has been found possible to effect a very favorable separation of zirconium from hafnium by an organic phosphate extraction using an acid aqueous zirconyl chloride solution. The stages from the liquid-liquid counter-current extraction were analyzed for zirconium, nitrate, hydrogen, and chloride concentrations. There appears to be a correlation between these factors and extraction efficiency.

The direct extraction of zirconium from the simple hydrochloric acid solution of the sodium zirconate produced in ore treatment was not feasible because of interface turbidity. This was caused by high silica content and prevented phase separations. Elimination of the silica through purification of this zirconium solution by the oxychloride crystallization however, permits satisfactory separation of the phases in liquid-liquid extraction. More consideration is being given to the effects of various salting out agents on the purification of zirconium from hafnium by liquid-liquid extractions employing tributyl phosphate solutions as the organic phase.

A number of diluents for the tributyl phosphate have been tested and none of those tested was decidedly better than butyl ether. Some highly chlorinated diluents gave densities for the organic phase greater than the aqueous phase. Attempts to use the salicylic acid and phthalic anhydride complexes of zirconium and hafnium in connection with this liquid-liquid counter-current solvent extraction were made. Separation was obtained with some other organic solvents but so far these are vastly inferior to the tributyl phosphate system of separation developed previously.

1.3 Preparation of Zirconium Fluoride

Considerable effort is being expended in attempting to determine a simple procedure for preparing a high grade anhydrous zirconium tetrafluoride from the wet process product $\text{ZrF}_4 \cdot \text{H}_2\text{O}$ described earlier. Prolonged exposures to dry HF gas at temperatures as high as 500°C have yielded good quality fluoride. Also plans are under way for scaling up the precipitation step to give 15 to 20 pound batches of the fluoride. Subsequent treatment of the hydrated fluoride in a rotary hydrofluorination furnace has been started and there seems to be some relationship between temperature of this treatment and the hardness of the metal prepared from the fluoride.

Since zinc is used in the reduction step for zirconium at the Ames Laboratory, it has been considered as possibly worthwhile in connection with fluoride preparation to try to obtain a double fluoride of zinc and zirconium. There was some hope that a wet process could be worked out that would yield an anhydrous double salt readily and thus remove the difficulty encountered with the $\text{ZrF}_4 \cdot \text{H}_2\text{O}$. So far, however, only a hydrate corresponding to about $\text{ZnZrF}_6 \cdot 6\text{H}_2\text{O}$ has been obtained with relatively low yields so this approach to solving the problem does not appear promising.

1.4 Experimental Bomb Reduction of Zirconium Fluoride

The small scale bomb reduction procedure has been fairly well standardized for testing the quality of materials employed in the process. However, miscellaneous experiments connected with the reduction of zirconium tetrafluoride to zirconium metal in the bomb are continuing. The quality of all materials employed in the reduction including the liner for the bomb are factors affecting the yield and quality of the final metal. In some reduction charges the detrimental effects of certain impurities can be largely

overcome by addition of certain materials or change in the ratio of the main constituents in the charge.

The dezincing operation is now usually combined with melting so it is employed only as a separate operation to give special sponge metal for arc melting.

1.5 Tin-Zirconium Alloy Preparation

Experimental preparation of tin-zirconium alloys by the bomb reduction process is continuing. A method of adding controlled amounts of tin, which gives a homogeneous alloy with low hardness and considerable ductility is being sought.

The general methods attempted are the following:

1. Adding tin during casting either to the dezincd zirconium sponge or to the zinc-zirconium biscuit. By this method controlled amounts of tin can be added but preliminary indications are that the corrosion rates and also the metal hardnesses are somewhat higher than with some of the other methods.

2. Addition of tin turnings to the bomb charge. In general, this method produces a softer metal than the above but only 60 to 70% of the added tin alloys with the zirconium.

3. Adding tin to the bomb charge, analyzing the biscuit and adding the deficient amount of tin during casting. This method will work but has obvious faults.

4. Co-reduction of ZrF_4 with various tin salts. Among those tried are SnI_2 , SnO and SnF_4 . Here also, approximately $2/3$ of the tin gets into the biscuit. The compositions and also the hardnesses are somewhat erratic.

1.6 Zirconium-Tin System

Work is continuing on certain details of the zirconium rich alloys containing tin. The compound at about Zr_4Sn can be obtained by careful heat treatment of alloys that have been produced by arc melting. However, these same alloys when remelted by induction in graphite do not respond to the heat treatment to give the compound Zr_4Sn . Only an alpha solid solution and a higher tin content compound result from this treatment. The explanation of

these observations is not known. Possibly the small amount of carbon (0.2 %) introduced in the melt on induction melting catalyzes the decomposition of the Zr_4Sn or perhaps the rapid cooling of the melt in the arc melting process sets up conditions favorable for its formation on subsequent heat treatment. Tests on graphite melted metal are to be made by arc melting a portion and determine its behavior on subsequent heat treatment.

Evidence so far obtained here indicates that the alpha solid solution contains at least 5 per cent tin.

1.7 Zirconium-Germanium System

This system is being investigated by sample preparation, thermal analysis, and X-ray studies of alloys containing from 0.2% Ge to 98% Ge.

Microscopic examination of the 7.7% germanium in zirconium alloy indicates that it is of eutectic composition. Its melting point was measured as $1540^{\circ}C$. Alloys in the region between 10% and 35% Ge show evidence of two compounds, one of which appears to be a peritectic compound. Previous X-ray studies indicated a compound at about 35% Ge and another between 35% and 100% Ge. X-ray studies of the peritectic compound are under way but have not been completed.

A series of anneals at temperatures between $1350^{\circ}C$ and $1600^{\circ}C$ have indicated an approach to one phase at about 17% Ge.

Thermal analysis of alloys containing less than 10% Ge by differential cooling rate studies previously indicated a solubility limit of less than 0.5%. A series of quenches at $1040^{\circ}C$ and $1450^{\circ}C$ show the 0.4% Ge-Zr alloy to be two phase at each of these temperatures.

1.8 Zirconium-Antimony System

The experimental work on the zirconium-antimony alloy system has progressed to a point where a report on the results of the investigation has been prepared. A compound identified as Zr_2Sb was found and investigated. The compound belongs in the hexagonal division of the hexagonal crystal class and the lattice constants are: $a = 8.394$ kX units and $c = 5.657$ kX units. The melting point of the compound is $1870^{\circ}C$. Other features of the phase diagram are reported elsewhere.

Some earlier observations on corrosion of zirconium-antimony alloys indicated that the low antimony alloys might not stand up well under prolonged exposure to 600°F water. However, more recent microscopic and weight change data indicate that alloys of low antimony (2% and less) in zirconium formed by co-reduction in a bomb and subsequently cast in graphite have desirable corrosion resistance to 600°F water. This resistance by antimony additions resembles quite closely that for tin in zirconium but the antimony content usually runs less than the tin in alloys with equivalent stability.

These corrosion resistant binary alloys of zirconium have been obtained by additions of tin or of antimony to make separate alloys. A program in which both antimony and tin are to be added to zirconium to form zirconium-tin-antimony alloys that are to be corrosion tested is being planned here. There is the possibility that tin and antimony will effectively supplement one another in increasing the corrosion resistance of zirconium.

1.9 Zirconium-Carbon and Zirconium-Oxygen Systems

Actual experimental determination of the behavior of zirconium containing carbon or oxygen has received little direct attention recently. Most of the effort has been spent in setting up equipment, preparing materials and working out procedures for systematic study of these systems under controlled conditions. Earlier experimental work had emphasized the importance of taking these steps because of the ease with which zirconium picks up oxygen.

1.10 Zirconium-Niobium Alloys

Further investigation of the resistance-temperature behavior of zirconium-niobium alloys has demonstrated that the 30 per cent niobium alloy does exhibit characteristics of a phase change. However, the action is extremely sluggish and the results are difficult to interpret. The 15 per cent alloy also shows pronounced anomalies but no explanation will be attempted until more complete information is available.

Additional microscopic study of the cast alloys of intermediate composition has indicated that a eutectic situation is more probable than diagram-wide solid solubility with a wide flat minimum region.

1.11 Corrosion of Zirconium Alloys

Zirconium alloys are being tested for resistance to corrosion in distilled water at 315°C (600°F). One series of these alloys consists of zirconium, tin and carbon made by melting iodide bar and tin in graphite crucibles in a high frequency furnace. The content of tin, nitrogen and carbon varied over wide ranges. The results after 200 hours are not consistent but indicate that carbon in excess of 0.5 per cent certainly cannot be tolerated and the acceptable limit may be much lower. Earlier work here indicated that 0.4% C might be the maximum.

Zirconium-antimony alloys that had been prepared by co-reduction in a bomb and then melted in graphite crucibles had a low rate of corrosion with a minimum of about 0.1 mg/cm²/mo. at 0.5 per cent antimony. Tests of the same kinds of alloys prepared by co-melting the constituents in graphite crucibles have not given consistent results.

2. Thorium

2.1 Metal Production

There have been recent further demands for thorium metal; however, our small development plant has managed to fill all urgent requests for metal to date. Some expansion of operations in the Metallurgy Building to give several times the original planned capacity for metal production is being made.

A group of engineers and other interested parties from the New York Operations Office, and Catalytic Construction Company spent several days at the Ames Laboratory going over the present process to obtain operational details for use in the construction of a pilot plant for thorium metal. This plant, estimated to cost between 2.5 and 3 million dollars, is being planned for the area near Cincinnati.

2.2 Experimental Thorium Fluoride Preparation

In the pilot plant operation thorium oxalate is precipitated from a nitrate solution. This oxalate is then dried and calcined to the oxide which is later treated with hydrogen fluoride gas to give thorium tetrafluoride. A number of tests have been made here to determine the feasibility of by-passing some of these steps from the nitrate to the fluoride.

The nitrate can be calcined directly to the oxide which can then be treated with hydrogen fluoride gas to give thorium tetrafluoride. The conditions for this process are being studied and the quality of the product being determined.

Thorium tetrafluoride can be precipitated from a solution of the nitrate by aqueous hydrofluoric acid. This short-cut to the desired product offers the advantage of a precipitation which should tend to give some purification in the preparation of the thorium tetrafluoride. The precipitate is the monohydrate which must be dehydrated before the tetrafluoride is usable in bomb reduction.

A rotary type continuous hydrofluorination reactor is being developed as a possible replacement for the stationary tray reactor now in the regular production hydrofluorination.

2.3 Experimental Thorium Reduction and Casting

Very little work was done in this quarter on the development of better charge or reduction conditions for thorium. However, tests on liner materials for the reduction charge indicate that high burned dolomitic oxide is not quite as good as our electrically fused dolomitic oxide which has been in storage here for about six years. Further tests are to be made on dolomitic oxide burned at a higher temperature.

Ceramic crucibles are being prepared for making some tests in an effort to find a more satisfactory material than BeO for melting thorium metal for casting.

2.4 Thorium Alloys

The investigation of physical and fabrication characteristics of thorium alloys is being continued. The weight of the experimental furnace charge has been increased to 125 grams from 75 grams and each charge is arc melted 4 times, as material melted only twice does not have as homogeneous a composition as is desirable.

Although some additional alloys with cobalt, manganese, aluminum and silver have been made, recent emphasis has been on chromium, molybdenum, titanium and zirconium. These four elements produce alloys that behave well in rolling even when considerable proportions are present. Under favorable conditions alloys containing 10 per cent chromium can be rolled cold; molybdenum alloys offer no difficulty in rolling but higher percentages of molybdenum show a tendency toward segregation; titanium may be added in excess

of 25 per cent without causing any difficulty in fabrication. Zirconium alloys are less amenable to fabrication; a 10 per cent alloy can be rolled cold readily but alloys from 15 to 30 per cent must be rolled hot in steel jackets. Fortunately, the hot rolled zirconium alloys show considerable ductility and a much reduced hardness.

In general, alloying appears to increase the softening temperature very little in comparison with the value for cold-worked unalloyed thorium taken from the production line but the ternary alloys with chromium and tin may constitute an exception to this statement. All alloys tested softened at 500°C, some of them to a considerable degree.

Measurements of electrical resistivity have been made on most of the alloys. The maximum resistivity found is not much more than 100 per cent higher than the value for unalloyed thorium. This increase is small in comparison with the changes that occur in some alloy systems.

Very few tensile tests were made on the alloys because an order for SR-4 strain gages was not filled until the end of the quarter. Considerable information on the mechanical properties of the alloys should be accumulated during the next quarter.

Although no attempt is being made to study the constitutional diagrams of thorium alloys at this time, some preliminary metallographic studies of sections of ingots indicate that none of the four elements being studied most thoroughly at the present time have much solid solubility in thorium. If any compounds are present they seem not to be of the brittle variety.

Several lanthanum-thorium and cerium-thorium alloys were prepared by dissolving thorium in molten cerium and lanthanum metals. Metallographic and X-ray examination of all of these alloys strongly indicate complete solid solubility of both lanthanum and cerium in thorium.

3. Vanadium Metal

Work on further developments for a production method for vanadium metal has been practically suspended for the time being. The major work in this direction recently has been connected with alloy studies where the vanadium metal employed has been produced by the production methods developed here earlier.

3.1 Vanadium-Titanium System

Investigation of the Ti-V alloys prepared by arc melting Ti sponge with V was continued. Further quenching runs were made on these alloys and X-ray data were obtained together with density and hardness values. Also melting point data have been obtained on a series of alloys.

Density measurements on the alloys prepared by co-reduction indicated that some contamination was present in the high Ti range.

A further series of alloys was prepared by arc melting; this time using V prepared here by reduction of V_2O_5 with Ca using an iodine booster, and the best grade of Du Pont sponge. In this series of alloys, the most interesting composition ranges were more fully covered than before.

The vanadium metal exhibits a melting point of around 1850°C while the titanium melts at about 1650°C . At approximately 25% vanadium a minimum of around 1525°C is found in the liquidus curve for these 2 metals. There seems to be complete solid solubility of these two metals in one another at high temperatures. The solid transition in titanium is lowered by the addition of vanadium and is perhaps brought down to room temperature by about 30% vanadium.

3.2 Vanadium-Aluminum System

Fusion of the pure components is not too satisfactory as a method for the preparation of aluminum-vanadium alloys. Solid vanadium has little tendency to dissolve in molten aluminum and aluminum tends to distill out of molten vanadium in a vacuum or even under helium.

However, a set of alloys has been prepared by arc melting under helium. These alloys ranging across the entire system from pure aluminum to pure vanadium show a progressive increase in density to the vanadium side. Microstructures are being interpreted along with other data, and further treatments will be employed to construct the alloy diagram. In addition some of the physical properties of these alloys will be studied.

4. Ceramics

The production of beryllia crucibles and parts for thorium casting required most of the effort in ceramics for this period. Furnaces and equipment for production have been overhauled to

facilitate this work. Some work in connection with a lime burning program of interest to the New York Operations Office was also performed. Near the end of the period some additions were made in the personnel of this group and we hope to get more of the needed development work back in the ceramics program.

5. Miscellaneous Problems and Equipment

5.1 Electrical Resistance Measurements at Elevated Temperatures

It has been shown that small amounts of impurities especially oxygen play a major role in distorting the true values of electrical resistance of metals at elevated temperatures. Therefore a prerequisite in electrical resistance measurements at high temperatures is a very good vacuum system. A vacuum system was built that maintained a vacuum of 10^{-7} mm even at high temperatures.

The potentiometric method for electrical resistance measurements is being employed. This consists of sending a very small current through the specimen and standard resistor which are in series and then measuring the voltage drop between two points on the specimen. From the value of the voltage drop across the specimen and the value of the current passing through the specimen the resistance of the specimen can be determined. Special equipment has been set up to obtain the experimental values.

5.2 Geiger Counter X-Ray Spectrometer and Goniometer

The new Norelco Geiger Counter X-ray spectrometer and goniometer after being installed had to be properly aligned so as to give correct angle readings and subsequently correct lattice parameters and structures of the specimens that are to be measured. This alignment was accomplished by adjustment of the goniometer until the values of the angles of the reflecting planes of a standard silicon specimen corresponded to the true theoretical values. With the goniometer scanning on the slow speed, $1/8^{\circ} 2\theta$ per minute, angles can be accurately measured to $\pm .005$ degrees and subsequently lattice parameters can be obtained with the accuracy of $\pm .005\text{\AA}$. If it is desired to just identify compounds and phases the goniometer can be operated at a fast speed of $2^{\circ} 2\theta/\text{min}$.

It was also desired to know what errors are introduced when the specimen is not in the plane of the specimen holder. Experiments were performed in which the specimen was below, above and tilted at various angles with respect to the plane of the specimen holder. It was shown from the results of these experiments that

one important factor in determining accurate lattice constants was that the specimen must be flush with the plane of the specimen holder.

5.3 Niobium

Some interest in the production of high purity niobium (columbium) here has led to some exploratory experiments on the treatment of niobium and tantalum ores and processes for their separation from one another. Niobium has a fairly low capture cross section for slow neutrons and it or some of its alloys might serve as material for use within a reactor where low capture, strength, high melting point, and/or certain corrosion resistance properties are desirable. Many of the ores containing these elements also contain rare earths and other materials of value such as uranium and thorium. The treatment of these complex ores with hydrofluoric acid appears to show some promise, however other procedures are to receive considerably attention. In connection with these problems, we plan to test liquid-liquid solvent extraction techniques on various separation steps.

6. Metallurgy of Rare Earths

See Page 22.

CHEMISTRY

Under the direction of F. H. Spedding, C. A. Goetz, C. V. Banks,
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Physical and Inorganic Chemistry Groups1. Separation of Rare Earths by Ion-Exchange

The heavy rare earths, Dy through Lu, are less abundant in general than are the lighter rare earths. It has been found that one of the richer sources of these elements is Norwegian gadolinite which contains about 40% R_2O_3 as mined. The oxides of this group are readily obtained by leaching the ground gadolinite ore with nitric acid, adding oxalic acid to the leachate in order to precipitate the rare earth group and igniting the resulting oxalate precipitate to the oxide at 800°C . The oxide consists of about 60-70% Y_2O_3 , 20-30% total light rare earths, 5-6% Dy_2O_3 , about 1% Ho_2O_3 , 3-4% Er_2O_3 , about 0.5% Tm_2O_3 , 3-4% Yb_2O_3 and about 0.5% Lu_2O_3 . In order to obtain these elements >99.9% pure, starting with such low initial concentrations, it is necessary to make two or three successive separations on ion-exchange columns. The pilot plant columns require an initial charge of 350-400 g. of R_2O_3 each per run. With 20 such columns in operation it is thus possible to process 7-8 kilograms of R_2O_3 per month. This means that the total amounts of Lu_2O_3 or Tm_2O_3 obtained in concentrated form each month is in the order of 40 g.; about 80 grams of Ho_2O_3 , 240 g. of Yb_2O_3 , 240 g. of Er_2O_3 and 450 g. of Dy_2O_3 are also obtained in concentrates at the same time. In order to accumulate enough material of a given composition for a column charge of 350-400 g. it is necessary to collect fractions over a fairly wide range for a number of months. During the past three months, three runs have been completed and a total of 23 kilograms of the R_2O_3 from gadolinite ore have been processed and the heavy rare earth fractions recombined into the fractions listed in Table I.

The new ion-exchange plant, being constructed in the Research Building is nearing completion and is expected to be in operation in the near future.

Table I
Enriched Fractions Obtained from Gadolinite Ore

Fraction		Weight R_2O_3 (g)
HRE #0	<50% Yb_2O_3 , >50% Lu_2O_3 + ThO_2	8.16
HRE #1	>60% Yb_2O_3 , < 50% Lu_2O_3 ; no Tm_2O_3	305.83
HRE #2	>80% Yb_2O_3 ; appreciable Lu_2O_3 and Tm_2O_3	202.04
HRE #3	>60% Yb_2O_3 ; < 50% Tm_2O_3 ; no Lu_2O_3	24.26
HRE #4	>50% Tm_2O_3 ; < 50% Yb_2O_3 + Er_2O_3	103.18
HRE #5	50-75% Er_2O_3 ; < 50% Tm_2O_3 + Yb_2O_3 ; no Ho_2O_3	57.82
HRE #6	75-95% Er_2O_3 ; < 25% Tm_2O_3 ; no Ho_2O_3	72.92
HRE #7	>95% Er_2O_3 ; < 5% Tm_2O_3 + Ho_2O_3	508.65
HRE #8	75-95% Er_2O_3 ; < 25% Ho_2O_3 ; no Tm_2O_3	110.38
HRE #9	50-75% Er_2O_3 ; < 50% Ho_2O_3 + Dy_2O_3 ; no Tm_2O_3	119.39
HRE #10	>50% Ho_2O_3 ; < 50% Er_2O_3 + Dy_2O_3	143.34
HRE #11	>50% Ho_2O_3 + Dy_2O_3 ; < 50% Y_2O_3 ; some Er_2O_3	192.67
HRE #12	>50% Dy_2O_3 ; < 50% Y_2O_3 ; some Ho_2O_3	148.93
HRE #13	20-50% Dy_2O_3 ; 50-75% Y_2O_3 ; some Ho_2O_3	530.15
HRE #14	10-20% Dy_2O_3 ; 80-90% Y_2O_3	3500.00

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2. Rare Earth Metallurgy

The major effort in this period has been to prepare rare earth metals for other laboratories. Shipments during this period included over one and a half kilograms of cerium, 150 grams of gadolinium and smaller amounts of lanthanum, neodymium and praseodymium.

Rare earth hexaborides have been prepared for use in one of the experimental physics groups of this Laboratory.

Extrusions of cerium and lanthanum have been carried out, although minor differences in samples used have prevented generalization of procedures.

3. Properties of the Rare Earth Metals and their Salts

3.1 Thermochemistry

During this period an improved model of a heat of solution calorimeter was assembled; preliminary tests on its operation were made. A new electronic timing-device was designed and constructed to record time within 0.001 second during electrical calibrations. A number of methods of bath-temperature control were investigated to improve the stability and sensitivity of the controlling mechanism. The method to be used gave an average deviation of less than 0.001°C from the set temperature. Pure chlorides of lanthanum, praseodymium, samarium, yttrium, and erbium were prepared for future heat of solution measurement.

3.2 Electrochemistry

Transference numbers, activity coefficients, and conductances of ErCl_3 solutions were determined. Within the concentration range of 0.001 M. to 0.034 M. , the cation transference numbers were found to lie between 0.448 and 0.414; the activity coefficients varied from 0.773 to 0.426. The distance of closest approach, a^0 , for Er^{+3} was calculated to be $5.65\text{\AA}$. Conductances of the chloride were measured between 0.0002 N. and 0.10 N.; the calculated equivalent conductances varied from 139.16 to 96.07 mhos. The limiting equivalent conductance was calculated as 142.3 mhos. These data are in general agreement with those previously obtained in this Laboratory for other rare earth chlorides.

4. Slurry Studies

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The spray burner apparatus (described in previous quarterly reports) for preparation of fine particle uranium oxide has been improved by installation of a 28,000 volt Cottrell-type electrostatic precipitator at the end of the collector chimney. This installation has increased powder yields approximately 20%.

Investigation of methods for the preparation of stable uranium slurries has continued. A slurry of properties somewhat better than the hot alkali-dispersed slurry previously reported was obtained by grinding uranium oxide powder (prepared by the spray-burner technique) into hot 0.5N NaH_2PO_4 and electrodialyzing the product. This slurry showed slight settling in 24 hours (readily redispersed by shaking), slight to moderate settling in 5 hours at 250°C (readily dispersed by shaking), a pH of 10, a viscosity of 9 to 10 millipoises at 30°C, and a specific conductance of 5×10^{-5} mho at 25°C.

Numerous "wet" methods for preparation of uranium oxide slurries have been investigated. The general technique which has shown most promise has involved fluxing uranyl nitrate in various molten salt mixtures. Of these, the most satisfactory results to date were obtained from a slurry prepared by fluxing uranyl nitrate with a mixture of NaH_2PO_4 and NaHCO_2 , (sodium formate) dissolving in boiling water and electrodialyzing the product. This slurry showed no noticeable settling in 24 hours, slight settling in 48 hours (sediment was difficult to redisperse), moderate settling in 5 hours at 250°C (readily redispersed by shaking), a pH of 8 to 9, and a specific conductance of 10^{-3} mho at 25°C. Investigation of slurries prepared by this and similar techniques is continuing.

5. Reaction Mechanisms

a. The precipitation of tetraphenyl arsonium permanganate and perchlorate has been under study from both an experimental and theoretical point of view. The latest results indicate that four ions, two of each cation and anion, constitute the nucleus upon which large crystals grow. The nuclei are assumed to be in equilibrium with the ions in solution at the start of the precipitation. ΔH for the formation of nuclei is on the order of -15 to -20 KCal, but ΔS is -50 to -80 entropy units, making the concentration of nuclei extremely small - hence a small number of crystals from a large number of ions.

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b. Work on the ceric-chloride reaction has disclosed that while the reaction is second order in CeCl^{+3} at high acidities, it is first order in CeCl^{+3} at low acidities. The work at high acidities allows calculation of the equilibrium and rate constants,

$$K = \frac{\text{CeCl}^{+3}}{\text{Ce}^{+4} \text{Cl}^{-}} \quad \text{and rate} = k (\text{CeCl}^{+3})^2.$$

The first order portion of the reaction has not been unraveled as yet.

c. The reaction between stannite and the cobalt II complexes has been completed. It was found that $[\text{Co}(\text{NH}_3)_6]^{+3}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ do not readily react with stannite, but $[\text{Co}(\text{NH}_3)_4(\text{OH})_2]^{+}$ and $[\text{Co}(\text{CN})_x(\text{NH}_3)_y]^{+}$ ($x + y = 6$) both react readily. This demonstrates that two OH^{-} 's and an undetermined number of CN^{-} 's will serve as electron transfer reagents, while apparently NH_3 's or one Cl^{-} will not so serve. Also stannous acid was shown to be monobasic and the ion HSnO_2^{-} was shown to dimerize, with

$$K = \frac{\text{Sn}_2\text{O}_3}{(\text{HSnO}_2^{-})^2} = 16$$

d. Work on the reaction of H^{+} with metals has shown that the rate of the reaction depends positively upon H^{+} , the metal surface, the ionic strength, and the presence of a complexing agent. The rate depends inversely upon the metal ion concentration. More data is being gathered to attempt to attach quantitative significance to these effects.

e. The reaction between Ti^{+3} and ClO_4^{-} is being studied, and the work on this system is almost complete.

6. Theoretical Calculations

Work on transition probabilities using the dipole velocity operator has continued with special reference to the OH and H_2^{+} molecules. These are designed as checks on the supposition that one can obtain moderately good wave functions by equating the dipole length and dipole velocity results.

Work has continued on the development of a powerful spark source. In connection with anticipated experimental results from use of this source, theoretical work has been begun on the theoretical expectations for triplet-triplet transition probabilities in benzene.

Several new attempts at measuring the singlet-triplet absorption of benzene at low temperatures have been made, but without success. Further improvements in apparatus and methods are being undertaken.

The literature survey of scintillation counters continues. During the next quarter it is hoped the group will progress to the point of setting up experimental apparatus for testing some new ideas for suitable scintillation counters.

Work has been started on a detailed theoretical study of the H_2O molecule using self-consistent-field procedures. At the present time the major effort is directed toward the evaluation of the necessary integrals. The group is cooperating in an international program on the computation of integrals useful for molecular quantum mechanical calculations.

7. Werner Complexes

Research was continued on infrared spectra of Werner complexes. Special emphasis is now being placed on preparative methods for obtaining pure specimens of the desired materials.

8. Calorimeter Studies

A new adiabatic shield for the hydrogen calorimeter was fabricated and as soon as installation of auxiliary equipment can be made the calorimeter will be put into service. Work in progress includes the fabrication of the thorium block, the calorimeter can, heater core and heat trap needed for proposed measurements on thorium.

The design of the helium calorimeter had been completed; the machine drawings for a simplified design have been submitted to the shop and fabrication is in progress.

9. Hydrogen-Uranium Equilibrium System

Investigation of the H_2 -U equilibrium system is nearing completion. Work with the HD -U and the D_2 -U systems has been started. Temperature control has been primarily responsible for slow progress in this program. Temperature must be controlled within $\pm 1^\circ C$ over a period of several months, and less than $\pm 1^\circ$ is highly desirable. To fulfill this need considerable effort has been

expended to develop an inexpensive, positive furnace temperature controlling system. While there is no data for the long-time experiments, temperature can now be controlled in a small furnace to $\pm 0.1^\circ$ (350 to 500°C range) for days and to about $\pm 0.5^\circ$ for several weeks with a new control device. The device has controlled furnace temperature to $\pm 0.01^\circ$ C for as long as eight hours.

10. Analytical Procedure for Oxygen in Metal

In the development of a method for determining oxygen in Ca metal it became necessary to determine how long to allow a given amount of metal to stand in an atmosphere of water vapor to react completely. Experiments were set up to determine the rate at which Ca and H₂O vapor react at 35°C, 40°C, and 50°C. It was hoped to get some idea of the nature of reaction in addition to the information necessary for the analytical procedure. Granular calcium was placed in a special apparatus at a predetermined temperature. The system was evacuated and then enough liquid water was introduced so that at the end of the reaction a liquid water phase remained in the apparatus. Ca metal came in contact only with water vapor. The rate of reaction was followed by observing the pressure of H₂ gas. Analysis of the data indicates that the reaction between about 15% and 95% completed may be best described by the law

$$f = k \log (1 + at)$$

where f = fraction Ca reacted; t = time in hrs., a = constant; k = rate constant. Reactions between Ca and D₂O vapor were also run using the same experimental set up. The reaction rate constant was lower, as was expected. Comparison of the rate constants at the three experimental temperatures is given below.

°C	$k \text{ H}_2\text{O}/k \text{ D}_2\text{O}$
35°	1.17
40°	1.18
50°	1.20

Additional experiments using 1:1 solutions of H₂O and D₂O are being planned to give possible information leading to substantiation of a hypothesized reaction mechanism.

11. Study of Inert Gas Purification Methods

Considerable data have been obtained to date which gives qualitative indication of the merits of a gas purification method, but no precise information has been obtained regarding flow rates, life of purifying material, character of material, size of bed and other possible variables. Experiments are now being set up to study these variables using synthetic gas mixtures of argon containing 5% total impurities. These impurities will be N_2 , O_2 , H_2O , CO_2 and hydrocarbons occurring in natural gas. Purifying materials under consideration include hot metals such as U, Zr, Ca, Mg, Fe, Zn; also materials such as P_2O_5 , $Mg(ClO_2)_2$, $CaSO_4$, $CaCl_2$, alkaline pyrogallol, vanadyl sulphate, ascarite, and soda lime.

12. Other Investigations

Work has been done on the synthesis of pure anhydrous chromium III bromide, iodide and fluoride, for use in an investigation of their magnetic properties. The chromium III bromide has been prepared. The synthesis of chromium III iodide has been attempted in an effort to get a pure compound; however, complete success has not yet been achieved.

A literature search for methods of preparing pure ThS has been made. It is proposed to study the heat capacity of ThS as part of a general program on the thermodynamics of thorium compounds.

Analytical Chemistry Group

1. Thorium

Work has been started on methods of analyzing thorium-aluminum alloys.

A new spectrophotometric method has been developed for the determination of trace amounts of aluminum in thorium. In this method the thorium is complexed with p-sulfobenzenearsonic acid, the iron is reduced with hydroxylammonium chloride and complexed with 1,10-phenanthroline, and the aluminum extracted with a chloroform solution of 8-quinolinol. The details of this method will be reported in the near future.

Reclaimed thorium metal has been analyzed for uranium by extracting the uranium with diethyl ether and then measuring the absorbancy of the thiocyanate complex. The method seems to be good to ± 0.5 ppm of uranium in thorium.

2. Zirconium

Zirconium-germanium alloys are being analyzed by distilling the germanium tetrachloride from a nitric-hydrochloric-sulfuric acid mixture. The germanium is collected in ice water and subsequently precipitated with tannin and ignited to the dioxide for weighing. The zirconium in the distilling flask is then precipitated with mandelic acid and ignited to the dioxide for weighing.

A further study is being made of the possible methods of analyzing zirconium-niobium alloys.

3. Service Analyses

At the request of the A.E.C. a sample of mixed rare earth chlorides from Brazil was analyzed for the various metals present.

A total of 2480 service analyses were made during the period of this report. The service analyses included: Commercial thorium nitrate for thorium and iron; thorium oxalate for thorium and iron; thorium oxide for thorium and iron; thorium fluoride for thorium, fluoride and iron; calcium metal for iron, manganese and nitrogen; dolomitic oxide for loss on ignition; thorium metal for iron, manganese, nitrogen, carbon and uranium; thorium slags for thorium and monazite sands and their solutions for total oxides (thorium plus rare earths), thorium, cerium and uranium; uranium oxides for uranium content; zirconyl chloride for zirconium, silicon and chloride; zirconium metal for iron, manganese, nitrogen, sulfide and silicon; methanol for water; rare earth metals for iron and nitrogen; uranium metal for nitrogen; vanadium metal for nitrogen; thorium-uranium alloys for thorium and uranium; rare earth mixtures for individual rare earths; germanium-zirconium alloys for germanium and zirconium; zirconium fluorides for fluoride and water; zirconium-antimony alloys for antimony and zirconium; zirconium-tin alloys for zirconium and tin.

Radiochemistry Groups

1. Ruthenium Complexes

Work on the ruthenium thiocyanate system has been completed. The data indicate only a one-to-one complex between thiocyanate

and ruthenium. The complex is the same whether tri- or tetra-valent ruthenium is the starting material. By analogy with the thiourea complex it is presumed that the ruthenium in the complex it is presumed that the ruthenium in the complex is Ru(III). The reaction forming the complex is independent of the hydrogen ion concentration and can be represented by the equation

The constant at an ionic strength of 3.0 was found to be 60 ± 1 .

The constants of the ruthenium-thiourea system were recalculated using a more exact mathematical analysis. The equations and the constants at this ionic strength were found to be

$$k = 16.3 \pm 0.5$$

$$k = 5.3 \pm 0.1$$

The ruthenium-dithiooxamide system is being investigated. It appears to resemble the thiourea system except that the complexes are considerably more stable.

2. Sulfur-Phosphorus Separation

Research is being continued on the separation of carrier-free phosphate from sulphate by ion exchange methods. Previously it had been found that a cation resin treated with ferric ion will quantitatively adsorb the phosphate in such a mixture while allowing the sulfate to pass through unaffected. The exact conditions for maximum separation and most efficient operation are now being obtained.

3. Coincidence Counter

A double windowless flow counter has been constructed which is suitable for coincidence counting with little or no absorbing

material between the sample and the counter. It is to be used to study the decay schemes of radioisotopes which give off very low energy electrons.

Since the emissions of Fe^{55} are of very low energy this nuclide was examined for coincidences. None were found even with no absorber on one side and only a thin backing on the other.

At present the decay scheme of Tl^{204} is being examined. Quite surprisingly there is a high coincidence rate at very low absorber thicknesses. Since the reported decay involves only a single beta-ray, this seems to be something new and previously unobserved. The cause of this high coincidence rate is being studied.

4. Chemistry of Recoil Atoms

The radioactive products of synchrotron irradiation are produced by (γ, n) , (γ, p) and similar processes in which a large particle (neutron or proton) is given off during the formation. Consequently, these isotopes have a much greater recoil energy than those produced by (n, γ) reactions in which only a gamma ray is given off in the formation process. The chemical effects of recoil might then be quite different in the two cases. While the effects from (n, γ) recoil have been studied extensively those from (γ, n) recoil have not. A program of study of such reactions has been initiated with organic halides as the subject. A fractionation column is being constructed in order to separate the various possible products.

Another research problem involves the use of organo-metallic compounds as target material for production of interesting isotopes. Organo-germanium compounds are the first which are being tried.

5. Activation Analysis

An activation analysis was run on three of the diamonds which are used in experimental physics for conduction counting (see page 45). Irradiation was done at the Argonne reactor and measurements were begun 8-10 hours after removal. By far the most prominent activity appeared to be Na^{24} as identified by its half-life, its decay energies and its high β, γ and γ, γ coincidence rates. A large part of this activity appeared to be on the surface. Two explanations appear possible. (1) Though the diamonds were thoroughly washed before irradiation and were handled

only with tweezers during and after this washing, it is possible that all of the salt contamination was not removed. (2) The diamonds were wrapped in aluminum and the Na^{24} may have been due to recoil atoms produced by the reaction $\text{Al}^{27}(\text{n}, \alpha) \text{Na}^{24}$. The latter explanation appears more likely and the next samples will be wrapped in a way which will avoid this possibility.

6. Preparation and Study of Radioactivities

Activities formed by synchrotron X-ray irradiations of platinum were studied. Periods of 80 m, 18 h and 4 d were found using the 70 Mev beam, and chemically identified as platinum. In the iridium fraction were a new 2.3 h activity and the 19 h Ir^{195} . The 2.3 h activity had a 1.0 Mev beta and was identified as Ir^{197} since it was the parent of the 18 h platinum activity which is well established as Pt^{197} . No osmium activities were detected. The 4 d platinum may be in part the Pt^{193} reported to decay by K capture. It is possible that some 4 d activity did form as a daughter of Ir^{197} although results are not conclusive as yet. Experiments have been planned which will indicate whether 80 m or 4 d periods are isomeric parents of Pt^{197} .

In irradiations of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ it was found that about 70 per cent of the platinum activity was retained as a complex ion. Preliminary experiments to indicate the chemical form of the other radioactive platinum have been undertaken.

The decay of radioactivities induced by photons in zirconium metal has been followed again in the positron-electron sorter with somewhat better performance of the instruments. Analysis of the decay periods are in Table II. An experiment is planned in which the activities produced will be chemically identified.

Table II

Activities Induced in Zr by 68 Mev Synchrotron Beam

Positrons		Electrons		Photons	
Half-Life	Intensity Counts/min	Half-Life	Intensity Counts/min	Half-Life	Intensity Counts/min
4.6 m	1790	4.3 m	10,000	4.4 m	2100
1.5 h	2390	1.8 h	320	6.8 h	60
5. h	340	5.8 h	1210	84. h	240
77. h	630	15.5 h	660		
		87. h	590		

7. Photofission Yields of Thorium

Determinations of photofission yields for thorium have continued. Tentative new yield ratios expressed in terms of atoms of the isotopes formed are: $\text{Mo}^{99}/\text{Sr}^{91} = 0.39$ and $\text{Mo}^{99}/\text{Br}^{83} = 0.95$.

Effects due to independent yields along a chain which will be required for total chain yields have not yet been considered. Such considerations will depend in part on the number of neutrons emitted per photofission which is not accurately known. The final fission yields may provide some information about this quantity.

8. Self Diffusion in Nickel

An apparatus has been constructed for the preparation of thin deposits of radioactive nickel on surfaces by the thermal decomposition of nickel carbonyl. A few deposits for self-diffusion and migration experiments have been prepared.

9. Inorganic Equilibrium and Kinetics

Solubility determinations of silver chloride in various chloride solutions have demonstrated the existence of $\text{AgCl}(\text{aq})$ and AgCl_2^- species. Equilibrium constants for their formation were obtained and measurements over a temperature range permitted the estimates of entropies for these species.

Kinetics measurements of the oxidation of the Mn^{III} iodate by periodate showed that a part of the MnO_4^- which formed rapidly was subsequently reduced slowly by iodate to give Mn^{IV} . Consequently, a study of the equilibrium between the Mn^{IV} - Mn^{VII} and the IO_4^- - IO_3^- complex appears possible.

Preliminary measurements for the disproportionation equilibrium of Mn^{III} in 1M HIO_3 to give Mn^{II} and Mn^{IV} yielded values of about 200.

10. Service Work

The preparation of samples for the physics division's beta spectrometers and other equipment continues. Experimental work in this connection has been continued on various Szilard-Chalmers types samples, notably organic chlorides.

11. New Space and Equipment

The new quarters for the Radiochemistry Groups in the Research Building have been partially occupied. A number of new pieces of counting and other measuring equipment have been set up, including two recording count rate meters and a recording vibrating reed electrometer. These instruments proved extremely useful in connection with the diamond activation analysis study.

X-Ray Chemistry Group

1. Metals and Alloys

In connection with the study of borides by the Metallurgy Group at this Laboratory, the borides of rare earths have been examined. In addition to the metal hexaborides, existence of CeB_4 and LaB_4 has been confirmed. For CeB_4 the tetragonal unit is $a_0 = 7.25$ $c_0 = 4.13$ Å. Metal positions have been determined.

Work is continuing on the structures of compounds of Th with the transition metals, particularly Co and Fe compounds.

2. Rare Earth Hydrates

Fourier projections onto (010) using signs determined by neodymium positions have given x and z parameters for all oxygens and sulfurs in monoclinic $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. The structure is being refined. Work is being renewed on $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. This work promises to shed some light on the variation in the behavior of rare earth ions in solution.

Other investigations of the group include work on electron deficient compounds, polyhalide ions, carbonyls and specific analytical reagents. Several structural determinations are in progress in each of these areas.

Spectrochemistry Group

1. Spectroscopic Methods for the Analysis of the Rare Earths

The development of spectroscopic methods for the analysis of purified rare earths has been continued. Emission spectrographic methods for the determination of other rare earth impurities commonly encountered in column-purified gadolinium, thulium, ytterbium, and lutecium are now under investigation.

2. Spectrographic Determination of Residual Impurities in Thorium Metal

A spectrographic method for the determination of residual impurities in thorium metal is being developed. The procedure is based on the overdamped condenser discharge excitation of conducting pellets prepared from thorium oxide-powdered flake graphite mixtures. Preliminary results indicate that all residual impurities of interest except fractional part-per-million quantities of boron, cadmium, and the rare earths can be determined in this manner.

3. X-Ray Fluorescent Spectroscopic Analysis of Hafnium-Zirconium Mixtures

Binary mixtures of zirconium and hafnium can be quantitatively analyzed by measurements of their X-ray fluorescent spectra. The fluorescent spectra are excited by irradiation of solid cylindrical disks of the mixed oxides by a beam of primary X-rays from a conventional X-ray tube. The intensity ratio of the lines

$$\frac{\text{Hf}_{L\alpha} + \text{Zr}_{K\alpha} \text{ (2nd order)}}{\text{Zr}_{K\alpha} \text{ (1st order)}}$$

is measured by a Geiger-Mueller tube and a conventional scalar counter. The concentration range covered with the present experimental set up is from 4% Hf, 96% Zr to 98.5% Hf, 1.5% Zr.

4. Miscellaneous Research in Progress

Other investigations in progress include (a) spectrographic determination of common impurities in calcium metal, (b) direct spectral line intensity measurements using photomultiplier tubes and associated electronic circuits, and (c) correlation of infrared spectra and chemical constitution.

5. Service Analyses

A total of 3073 service spectrographic analyses were completed during this period. The samples consisted primarily of rare earths and zirconium-hafnium fractions, and calcium, thorium, and zirconium metals.

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6. Excitation Stand Development (Weber*)

An excitation stand, designed for use by the Spectrochemistry Group, has been laboratory tested during this period. Modifications were made, including the replacement of the bakelite back by a transite backing necessitated by the excessive heat generated. The device met all requirements and will be in operation immediately.

The projection lamp for use with the excitation stand is in the fabricating shop at this time. Optical equipment for the above is under consideration.

7. Scanning Mechanism for Spectrometer (Weber*)

The scanning device described in ISC-137 has gone through the design stage. Working drawings have been completed and have been submitted to the shop. The device will be ready for testing shortly.

8. Voltage Integrator Device (Weber*)

The design of a mechanical voltage integrator drive mechanism has been completed and is ready for fabrication.

* Work performed with the cooperation of the Department of Architectural Engineering.

PHYSICS

Under the direction of G. W. Fox, J. F. Carlson, G. C. Danielson, D. E. Hudson, E. N. Jensen, J. M. Keller, J. K. Knipp, L. J. Laslett, S. Legvold, G. H. Miller and D. J. Zaffarano

Theoretical Physics1. Ionization and Excitation by Electrons

A general theoretical treatment of the statistics of the excitation and ionization by electrons in their passage through a gas has been developed which leads to non-homogeneous linear integral equations for the moments of the statistics, which are the average ionization or excitation and the mean square fluctuation in the ionization and excitation, etc. Two problems which present themselves are: (1) the simplification of the resolving kernel of the equations and (2) the boundedness of the change in the average ionization expected resulting from a single collision. No satisfactory solution of these two problems has been found. Simplifications are being sought.

2. Ionization by Heavy Particles

A generalized treatment of the ionization produced by a particle which is stopped in a gas has been developed and an interpretation of the probability coefficients which enter in the theory is being sought.

3. Radiation in Pi-Mu Meson Decay

A pi meson at rest can decay into a mu meson and a neutral particle of zero mass. If E_0 is the energy of the mu meson in normal decay, the probability that a gamma ray be emitted and the mu meson have energy in the range E to $E + dE$ is estimated to be

$$\frac{e^2}{E_c} \frac{1}{\pi} \sqrt{\frac{E}{E_0}} \frac{1}{E_0 - E} \frac{4}{3} \frac{E}{\mu c^2} dE$$

The probability that the meson have energy less than $\frac{2}{3} E_0$ is found to be of the order of $1/25000$.

4. Specific Heat of Rare Earth Metals

The rapid fall of specific heat on the high temperature side of the low temperature specific heat maxima must indicate some coupling between the electrons of different atoms, beyond that provided by the averaged electrostatic fields with the same symmetry as the crystal. Possible sources of such coupling are:

- a. direct electrostatic interaction between f electrons of neighboring atoms.
- b. direct spin interactions between f electrons of neighboring atoms.
- c. electrostatic exchange between f electrons of neighboring atoms
- d. exchange interactions between f electrons and conduction electrons
- e. coupling of electronic and vibrational motion.

Item d is of particular interest in view of Zener's recent theory of ferromagnetism and crystal structure based on this interaction. Some effort was devoted to this type of interaction, but without result. A representation of the conduction electron wave functions as plane waves will give no coupling. Determination of the departure of the wave functions from plane waves by perturbation methods is of doubtful validity (though perhaps one should attempt the calculation anyway). We have been unable to think of another approach, short of a serious attempt to calculate conduction electron wave functions.

The low degree spherical harmonic components of electrostatic fields in a hexagonal close packed crystal have been determined. For the point charge model considered (no electronic screening), the magnitude of the Y_2^0 and Y_3^0 terms was calculated at one ratio of lattice parameters, and also the derivative of the coefficients with respect to the axial lattice parameter.

5. Gamma Induced Nuclear Reactions

The relative frequency of (γ, n) and $(\gamma, 2n)$ reactions was studied, particularly in connection with Dr. Sagane's¹ experiments on Cu^{63} bombarded by the synchrotron. The following assumptions were made:

¹Visiting Professor from Tokyo University; at present at the Radiation Laboratory, University of California, Berkeley, California.

- a) One neutron was evaporated from the excited nucleus. For a given gamma ray energy, the neutron could have any energy up to the maximum available. The distribution in neutron energy was assumed Maxwellian with a temperature corresponding to the excitation of the nucleus.
- b) Whenever the residual energy of the nucleus was sufficient to allow escape of another neutron, the second neutron did come out.

The theoretical ratio of two-neutron to one-neutron reactions was too large, particularly at high gamma energies. This suggests that, besides being an over-simplification, the calculation underestimates the probability of an outcoming soft quantum competing with (second) neutron emission.

An attempt was made to modify the theory of Weisskopf and Ewing² for (γ, d) processes to explain the relative frequency of protons and deuterons emitted from copper.³ Neglecting the question of existence of pre-formed deuterons within the nucleus, both the smaller density of final states of the residual nucleus and the greater barrier reflection makes the observed frequency of deuteron emission difficult to understand. The likelihood that the effective radius of a nucleus for deuteron emission is greater than for proton emission, and some shielding effects due to the two-nucleon nature of the deuteron, are not sufficient to bring agreement with experiment. (The shielding effects were suggested to us by Dr. L. Katz of Saskatchewan.) The behavior of a deuteron in an electric field that acts only on the proton component is, by itself, an interesting and difficult quantum theory problem.

The excess of protons over neutrons produced by gamma bombardment of ^{64}Zn (experiments of Katz and Cameron reported to us by Dr. Katz) can be understood if one takes into account; a) reduction of (γ, n) processes by competition from (γ, np) processes, and b) the lower threshold for proton emission. The predicted ratio of (γ, p) to (γ, n) processes was in good agreement with experiment.

6. Service to Other Groups

The Theoretical Physics Groups continue to serve in an advisory capacity to the Experimental Groups of the Laboratory on numerous basic and applied problems.

²Weisskopf and Ewing, Phys. Rev., 57, 472, 935 (1940).

³Byerly and Stephens, Phys. Rev., 83, 473 (1951) and Warren Smith of this Laboratory.

Experimental Physics

1. Radiation Studies

1.1 Beta-Spectra of P^{32} and P^{33}

The work on the beta-spectra of P^{32} and P^{33} was essentially completed during this period. A detailed report of this work is found in Report ISC-157.

Additional work will be done on this problem when a sulfur sample enriched in S^{33} is obtained from Oak Ridge.

1.2 Calibration of Thin Lens Spectrometer

Just prior to this report period a short-circuit developed in one of the eighteen coils of the thin-lens spectrometer due to condensation of moisture. The spectrometer has now been recalibrated for various arrangements.

1.3 Intermediate Image Spectrometer

The construction of the intermediate image spectrometer has been completed. Using the internal conversion line of Ba^{137} , the optimum operating conditions of the spectrometer have been determined for three energy ranges. This involved determining the shape of the magnetic field and the positions of the source and counter in order to give optimum operating conditions as determined from the resolution and relative intensities of the conversion lines. In addition the effects of the opening of the center baffle, source diameter, and position of a second baffle between the source and the center baffle were also studied.

Since the spectrometer is enclosed in iron it is important to determine whether there is a linear relationship between the momentum of the focused electrons and the current in the spectrometer coils. In the range 0.150-2.5 Mev the relationship appears to be quite linear. Further work must be done below 0.15 Mev and above 2.5 Mev in order to determine its linearity in these ranges. The spectrometer has been calibrated by means of the conversion lines in $Th(B,C'')$.

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A low pressure G-M counter for the spectrometer has been developed which gives an 80 volt plateau with a 7.5% rise per hundred volts, operating at 10 cm of mercury. This counter will make possible the use of thin counter windows.

Work has also been started on the circuits for a scintillation spectrometer which will be designed specifically for the purpose of doing coincidence work and is to be used on one end of the intermediate image spectrometer.

1.4 The Radiations of Ag^{112} and Ag^{113}

With the completion of the intermediate-image magnetic beta-ray spectrometer, definite plans have been made to attempt the use of this instrument for the examination of radiations from synchrotron-induced radioactivities. The spectra of Ag^{112} and Ag^{113} , produced by the irradiation of cadmium nitrate, will be the first of such activities to be studied. To permit the attainment of optimum irradiation conditions in the preparation of such sources, a preliminary study was begun to measure the decrease of induced activity with depth in a sample exposed to the synchrotron beam.

1.5 Radioactivities Induced in Zirconium Metal by Synchrotron Irradiation

The numerous periods induced in pure zirconium metal when exposed to synchrotron X-radiation have been studied. This work, done in collaboration with the Radiochemistry Group, makes use of a large water-cooled coil for separation of the electron and positron activities with reasonable efficiency. The plans for the immediate future include radiochemical analysis of the active products, in an attempt to assign definitely the various periods now obtained. This program may aid in assessing the practicability of activation analysis of the metal.

1.6 Investigation of Scintillation-Counter Performance

The comparison of the performance of various scintillation-counter designs has been resumed. This work is of importance in implementing the measurement of radiations from synchrotron-induced radioactivities with reasonable reliability and is expected to prove of future value in connection with counting experiments which may be undertaken during the irradiation. Recently some attention has been given to liquid scintillators in connection with this program.

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1.7 Synchrotron

The magnetic field of the synchrotron appears to be such that, with the equipment in its present condition, a significant improvement in intensity is obtained by the use of two additional pairs of compensation coils. The controls for these have now been permanently installed at the desk and connected. Progress has been made on the construction of a new oscillator unit and some attention devoted to the problems of decreasing the R. F. power slowly, when desired for protraction of the beam in connection with counting experiments. The present glass vacuum chamber ("donut") has been in steady use since the synchrotron was first put into operation and now exhibits rather poor conductivity over certain areas of the interior wall. For this reason an initial trial of the ceramic donut which has been constructed here was attempted; the new donut proved to fit nicely between the magnet poles but further tests have been deferred due to vacuum difficulties.

2. Nuclear Studies

2.1 Fission Fragment Experiment

Several pulse height distributions have been made for fission fragments thus far. The first distributions proved to be unreliable due to electronic equipment failure. More recently a distribution has been obtained in argon which seems to agree very well with published distributions. Several more distributions will be made in argon under different conditions to be certain that saturation conditions have been attained. It is expected that distributions in helium will be taken very shortly.

The chamber itself now seems to be in very good shape. The purifier is working very well, and the chamber is quite tight. Trouble has been encountered in the circuit which produces calibration pulses for the amplifier. Some of the precision resistors in this circuit have drifted rather badly and all are being replaced with better resistors.

A little additional work has been done on the technique for spraying on uranyl nitrate films. A device has been constructed using a potassium iodide crystal and a photomultiplier tube which scans the surface of such a film and counts alpha particles from representative areas. A film may thus be examined in a reasonable length of time for uniformity. It is now felt that films can be made to almost any area density to about one per cent uniformity. There is still some concern about the uniformity of the films on

a microscopic basis. At the present various means are being considered for checking this. It is probable that a method of optical interference similar to that used for checking the uniformity of thin organic films will be used.

2.2 Low Energy Experiments

The determination of the secondary electron yield from various surfaces under positive ion bombardment has been completed. Briefly, some of the conclusions follow.

- (1) It is very important to have a smooth clean surface on the sample to be measured. When the sample is placed in the vacuum system it should be kept at an elevated temperature. It is essential that it be heated up before it is bombarded.
- (2) Diatomic and triatomic ions may be regarded as two and three separate monatomic ions which share equally the initial energy.
- (3) Clean, smooth surfaces of pure metals all seem to give rather low secondary yields. Some alloys give high yields, and dirty surfaces usually give large secondary to primary ratios. Orders of magnitude are about two electrons per primary ion for clean pure metals and about six for dirty surfaces.

In the experiment to measure the stopping power of thin organic foils, the housing for the electrostatic analyzer has been machined and is being vacuum tested. The foil chamber, with its rotating seal, and the scattering target chamber is in satisfactory condition.

The large proportional counter, which is to be used in several experiments, has been operated satisfactorily.

In the proposed experiments to measure the energy per ion pair for various bombarding particles in various gases, the preliminary design work has been done and construction has begun.

2.3 Kevatron Operation

The corona shield for the ion source, mentioned in the previous report, has been installed. The beam has been analyzed, using the magnetic analyzer. For hydrogen, the atomic component seems to be only about ten per cent. The diatomic and triatomic components predominate, and under the usual working conditions are about equal. The triatomic component is very pressure-sensitive, which is not true of the other two. The identification of

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the components is fairly definite, both from the magnetic field ratios and from the secondary electron yields from each component. A large triatomic yield has also been found by a group at Los Alamos.⁴

2.4 Cloud-Chamber Study of Possible Photodeuteron Processes

The 12-inch cloud-chamber has been employed to demonstrate the production of a substantial number of deuterons in the irradiation of metallic copper with synchrotron X-rays. The identification of a deuteron group was accomplished by determining the mean magnetic curvatures shown by the tracks in a fixed range interval a definite distance from the end of the track. Despite the use of helium as the permanent gas in the cloud chamber, scattering played, of course, an important role in this work. The effect of scattering was determined both by computation and by means of an auxiliary, control experiment in which protons produced by neutron-recoil were present exclusively.

The results of the measurements led to a curvature-distribution for the particles emitted in the irradiation of copper in which the presence of a deuteron component could definitely be noted and the relative number of deuterons estimated. This conclusion,⁵ provides a significant confirmation of the photodeuterons reported from copper in the work of Byerly and Stephens⁶ with nuclear photographic emulsions.

It is planned to make a similar search for photodeuterons from other materials and preparations are underway to permit the use of sulfur as a target. Sulfur is of perhaps special interest since evidence⁷ of another nature, based on the character of the activation curve for the formation of p^{30} and s^{32} , suggests that a marked number of photodeuterons may be expected. Some relatively minor modifications of the cloud-chamber equipment have been made with the aim of implementing this future work.

⁴LA-1260

⁵W. H. Smith, Bull. Amer. Phys. Soc. 26, #6, p. 32, Paper M7 (October 24, 1951).

⁶P. R. Byerly, Jr. and W. E. Stephens, Phys. Rev. 83, 54 (July 1, 1951).

⁷E. L. Harrington, L. Katz, R. N. H. Haslam, and H. E. Johns, Phys. Rev. 81, 660(A) (February 15, 1951).

2.5 Measurement of Photonuclear Activation Curves

The program for the determination of the variation of cross-section with energy for photonuclear reactions produced by the synchrotron has been continuing, again along three somewhat different lines. The work performed up to the present time has exclusively considered the detection of photonuclear reactions through measurement of the resultant radioactivity; the possibility of observing other photonuclear reactions by the counting of heavy particles produced during the irradiation is, in this Laboratory, just now beginning to receive attention.

a) Dr. Sagane¹ has continued to obtain activation curves for a variety of different photonuclear processes and the inference therefrom of approximate cross-section curves, using the procedure he developed and of which brief mention has been made in the preceding quarterly report (ISC-171).

b) Mention has been made in previous reports to the use of an oscillating pair of samples, with the beam energy switched to a definite reference energy when one of the samples is in position in the X-ray beam. It has been found inappropriate to attempt the analysis of activation curves obtained in this way solely with the aid of theoretical curves for the relative magnitude and spectral shape of the synchrotron output. The method appears to be quite convenient, however, for obtaining activation curves which may be analyzed with the aid of some secondary standard. The results so far acquired may be said to lead to the following conclusions with respect to the method: i) Interesting information may be obtained concerning the variation of beam output with energy, the injection conditions remaining fixed, if one assumes the cross-section curve for some specific photonuclear reactions to be known (as, e.g., that for the $\text{Ag}^{107}(\gamma, n)\text{Ag}^{106}$ reaction); ii) cross-section curves which have been reported for diverse photonuclear reactions may be intercompared for mutual consistency, and satisfactory consistency has in this way been found between the results for Ag, Cu, and C published by other laboratories; iii) with the aid of a reliable cross-section curve for one suitable reaction, considered to be sufficiently well known to serve as a secondary standard, or supplemented by accurate information concerning the variation of quantum output with synchrotron energy (vide infra), the present method affords a particularly convenient way of determining other cross-section curves without further careful attention to the beam-monitor problem.

c) The magnetic analyzer, constructed to permit a direct means for monitoring the synchrotron yield at a definite quantum energy, has been subjected to initial performance tests. The results of these tests suggested that some modification of the

original installation and associated electronic devices be made and these changes are now being carried through. As indicated previously, it is believed that this device, if it is made trustworthy, will prove to be a particularly suitable and direct type of monitor; in addition, the experience and equipment obtained with it may subsequently prove of value in possible future counting experiments to be performed in the presence of the X-ray beam of the synchrotron.

2.6 Studies with Nuclear Photographic Emulsions

Initial steps have been taken to apply nuclear photographic emulsions to the detection and energy measurement of protons emitted in certain photonuclear reactions.

a) Apparatus has been set up, and provisionally tested, to permit the detection of photoprotons emitted at various angles from suitable foil targets. It is hoped that results to be obtained with such an arrangement will permit the measurement of possible high-energy anisotropic proton groups, which are of particular interest in connection with some theories of photonuclear processes.

b) A chamber has been designed to permit the irradiation of a gas, under pressure, in the synchrotron beam and the detection in nuclear emulsions of any photoprotons which result. It is hoped that the proton yields obtained will permit the photodisintegration of deuterium to be examined in this way, since the disintegration of the deuteron would appear to be particularly simple and significant theoretically.

3. Solid State Physics

3.1 Diamond Counters

Rectification effects in diamond have been investigated in detail. The degree of rectification and even the direction of rectifications depends upon the particular diamond used and the previous history of the diamond. However, two effects appear to be fairly general. First, a diamond which exhibits large rectification in its counting properties also seems to exhibit large rectification in its photoconducting current. Second, if a positive probe gives a higher counting rate than a negative probe, a positive probe will also give a larger photoconducting current. Furthermore, there appears in all diamonds to be a decrease in rectification with frequency of the alternating voltage

in the photoconductivity experiments. This decrease has been studied quantitatively and is found for many diamonds to begin to occur in the frequency range 10^3 to 10^5 cycles per second.

Small amounts of impurities in diamond are probably responsible for all electrical conduction processes in diamond (including the phenomena of conduction counting and photoconductivity). These impurities may consist either of foreign atoms or of lattice defects. No method of examining the nature of lattice defects in diamond has been suggested. If foreign atoms are present, however, it is conceivable that the atoms might be identified by activation analysis. Three diamonds were sent to Argonne and bombarded for one week with neutrons inside a reactor. The diamonds were returned to Ames and decay curves taken by the radiochemistry group. Sodium was positively identified but much of the activity was lost upon washing. Therefore, the observed activity is probably the result of surface contamination.

3.2 Sodium Tungsten Bronze

The electrical properties of sodium tungsten bronze have been reported previously. These compounds have the interesting property that the concentration of free electrons is equal to the concentration of sodium. Hence we have a metal in which the Fermi level and properties dependent upon the Fermi level can be varied over wide limits.

One such property is the color of the crystals. With increasing sodium content (and hence increasing Fermi level) the color changes from blue to red to yellow. Two explanations of this color change are possible on the basis of free electron theory. The color change from red to yellow can be accounted for using the classical dispersion theory of free electrons as suggested by Zener to explain the transparency of alkali metals in the ultraviolet. This theory was applied successfully in this Laboratory to the change in color with concentration of lithium dissolved in liquid ammonia. The color results from selective reflection. An alternate explanation uses the band theory of solids; the color results from absorption of the complementary color when electrons are raised in energy from the filled band to the surface of the Fermi sea in the conduction band. This concept has been used by Mott and Jones⁶ to explain the color of copper and brass.

⁶"Properties of Metals and Alloys", by N. F. Mott and H. Jones, Oxford Press (1936), p. 119.

In the case of sodium tungsten bronze the cutoff wave length on the basis of the classical theory would occur in the ultra-violet rather than in the visible as required to explain the color. Furthermore, thin red films produced by sputtering Na_xWO_3 are red rather than bluish-green by transmitted light as required by selective reflection. An absorption spectrum taken by the Cary Recording Spectrophotometer shows all wave lengths absorbed except the red and thus indicates selective absorption to be the explanation of the color. Experimental evidence thus appears to support the band theory rather than the classical theory in accounting for the color change from red to yellow. If this is true, it should be possible to investigate the band separation as a function of sodium concentration, which would be of great assistance in a theoretical examination of the wave functions and potential distribution for the perovskite structure.

The absorption spectrum of the red film of Na_xWO_3 shows also complete absorption (or reflection) beginning at about 3000 Å. This may be the result of electrons being raised in energy from the Fermi level to the next higher band (or Brillouin zone).

3.3 Thermal Conductivity of Metals

A new method of measuring the thermal diffusivity (and hence the thermal conductivity) of metals has been developed. This method is a combination of King's method and Starr's method but uses only one period of the heat wave transmitted through the specimen. The method is inherently faster, simpler in computation, and of greater reliability. The method has been applied to copper and to thorium in the temperature range 20°C to 500°C. The results for copper indicate an accuracy of about one per cent which is probably better than any previous measurements of thermal conductivity as a function of temperature in this temperature range. The results for thorium are not quite so good at elevated temperatures but are still being improved.

3.4 Low Temperature Research

a. Construction of Equipment.- During this period considerable difficulty was encountered with the liquid air apparatus. The lines would become blocked soon after the apparatus was started. The difficulty was finally traced to the sodium hydroxide scrubbing tower which was found blocked with calcium carbonate and dry sodium hydroxide, making carbon dioxide removal nearly impossible. As a consequence of the air difficulties only minor progress was made on alterations which initial tests dictated for the hydrogen liquifier.

The 20 kilowatt electromagnet, was completed and tested. It was found that the magnet equipped with iron pole pieces would produce a magnetic field of the order of 17.5 kilogauss for a 2.6 inch pole gap and a field of the order of 20 kilogauss for a 1.5 inch pole gap. In the course of the initial runs it was found that the kerosene-water heat exchanger was leaking, making it necessary to design and build a new exchanger. The new unit proved satisfactory. Still to be completed were the cobalt pole pieces for the magnet, which should give at least a 10% higher field for the magnet.

Apparatus for use in conjunction with the electromagnet in determining the Hall Coefficients of rare earth metals were designed and construction of the equipment has been initiated. The principal constituent parts are a 100 cycle/sec signal generator and an amplifier tuned to this frequency.

b. Research.- X-ray analyses of the crystal structures of a number of rare earth metal samples at room temperature indicate that many of the metals are mixtures of hexagonal close-packed micro-crystals and face-centered cubic micro-crystals. In the case of Ce it was found that the cast metal was mostly face centered cubic with some hexagonal whereas extruded metal was almost entirely face centered cubic. Results on Ce also indicate that when samples are cooled down to 4°K there is a tendency for more hexagonal crystals to appear when the samples are brought up to room temperature again. This information on the crystal structure is proving useful in attempts to understand the behavior of the electrical resistivities of the metals at low temperatures. A table of the X-ray results follows:

Table III

Metal	Preparation	Crystal Structure
La	Cast and turned	hexagonal close packed and face centered cubic
La	Extruded and turned	hexagonal close packed and face centered cubic
Ce	Cast and turned	face centered cubic with hexagonal close packed
Ce	Extruded and turned	face centered cubic
Pr	Cast and turned	hexagonal close packed with a small amount of face centered cubic
Nd	Cast and turned	hexagonal close packed

Results of tests on the magnetic moment of gadolinium metal indicate a saturation magnetic moment of 243 c.g.s. units. This result is tentative inasmuch as only weak magnetic fields have been available for the analysis.

3.5 Heat of Vaporization of Rare Earths

A study of the latent heats of vaporization of rare earth metals has been continued. The method involves measuring the relative rate of evaporation of atoms from the molten metallic surface as a function of temperature. Application of the mass spectrometer to study the atomic beam is unique. The spectrometer beam current is proportional to the rate of evaporation in the apparatus used. A plot of the logarithm of the beam current versus the reciprocal of absolute temperature gives the latent heat by the Clapeyron relation of thermodynamics.

Most of the work so far has been with neodymium. Preliminary results give good straight-line plots for individual runs of beam current versus temperature. The slopes are reproducible between runs to within plus or minus six per cent of the average latent heat of about 86 kilocalories per mol, measured in the temperature range from 800°C to 950°C. However, it appears that the fluctuations may not be random, and work is in progress to effect improvement in the reproducibility of the data.

Recently measurements have been started on the latent heats of lanthanum and praseodymium. Results on these metals can be compared with the latent heats measured in this Laboratory. The comparison will be valuable because it will be the first time that the heats of vaporization of highly purified rare earths have been measured by independent means.

3.6 Electrical Properties of Crystalline Boron

A study is under way on the measurement of the Hall effect and conductivity of single boron crystals as a function of temperature. Measurement of these quantities yields important information concerning the number and mobility of current carriers in the solid. The temperature dependence of the number of carriers leads to an activation energy for the material as a semiconductor. Two methods of attack are being investigated. The first is centered about the production of single boron crystals large enough to allow the use of conventional techniques. The second is based on the use of the very tiny crystals which can be grown by methods known at present.

Most of our attention has been concentrated on the second method and the work constitutes an extension of some preliminary studies.⁹ True micromanipulation techniques are required since the crystals on the average are only about 0.006" long and less than half as wide. An improved method of mounting single crystals with two end electrodes has been developed and conductivity measurements are under way. Several methods of adding two or three additional electrodes for the Hall measurements have been tried, and the results promise to evolve into a successful technique.

⁹Shinn, Iowa State College Thesis (M.S. 1950).

ENGINEERING

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Under the direction of G. H. Beyer, G. L. Bridger,
E. S. Fitzsimmons, W. R. Millard, G. Murphy
B. F. Ruth and M. Smutz

Chemical Engineering Groups

1. Production of Thorium from Monazite (G. L. Bridger, G. H. Beyer, C. O. Frush, M. E. Whatley, K. G. Shaw, J. H. Bochinski)

ISC-170, "Production of Pure Thorium and Uranium Compounds by the Acid Dissolution of Monazite Sand" by Bridger, Shaw, Whatley and Bochinski, September 21, 1951, includes a discussion of the process design variables that have been investigated to date.

Laboratory data obtained on the extraction of aqueous thorium nitrate, using tributyl phosphate as solvent, have confirmed the desirability of keeping the sulfate ion concentration low. The direct extraction of thorium from monazite-sulfuric acid solution also appears attractive from the preliminary data obtained. Further investigation of the new technique of lyometallurgy--a leaching process employing an organic solvent--shows promise for removing the thorium from the digested sand without the necessity for fractional precipitation.

The procurement of equipment for obtaining engineering data on a pilot-plant scale is well under way. As soon as the new Research Building can be occupied it is planned to process several hundred pounds of Idaho monazite for its thorium and uranium content. A process for the separation of pure cerium and lanthanum from the rare-earths contained in the monazite is also under development.

2. Production of Zirconium by Adsorption (G. H. Beyer, R. H. Giffen, J. B. West, R. B. Edwards)

The removal of hafnium from solutions of zirconium by adsorption on silica gel has been complicated by air entrained with the gel causing breaks in the 60" high column of gel used. Installation of a 30 rpm stirrer in the upper part of the column was found to liberate most of the entrained air and eliminate the breaks and channeling difficulties caused by the air.

From a series of 120-hour runs on the continuous silica gel adsorption column it has been possible to obtain the engineering data necessary for the design of larger columns. The major variables in the design of larger adsorption purification columns were found to be: (1) the ratio of the volume of the silica gel bed to the volume rate of withdrawal of purified product solution, (2) the ratio of the mass of hafnium per hundred parts of zirconium in the feed solution to that in the product solution, and (3) the ratio of the weight rate of silica gel addition to the volume rate of withdrawal of purified product solution.

The design information was applied to obtain an estimate of the size and cost of a semi-works plant for producing one thousand pounds of hafnium-free (≤ 500 ppm hafnium) zirconium per month. A 17-foot high column with a cross-sectional area of one square foot was estimated to be adequate; capital costs of \$70,000 would permit purification of zirconium tetrachloride to hafnium-free zirconium oxychloride octahydrate at a cost of \$6.65 per pound of zirconium purified. A current competitive process -- the thiocyanate extraction process used at Oak Ridge National Laboratory -- was estimated to cost \$10.14 per pound of zirconium purified, at the same scale of operation (1000 lbs. zirconium per month). Although both processes promise considerable reduction in cost as plant size is increased, there is no reason to believe that changing the scale of operations would adversely affect the favorable cost comparison for the silica-gel process.

3. Liquid-Liquid Extraction Equipment Studies (G. H. Beyer, N. Barson, R. Cohen)

The need for improved designs of liquid-liquid contacting equipment has been accentuated by the A.E.C. program for the production of extremely pure metals. A study of the operating characteristics of a Podbeilniak centrifugal contactor and a pulse extraction column has been inaugurated, in the hopes that such equipment may prove useful in solvent extraction problems confronting the Ames Laboratory.

4. Fundamental Studies of Liquid-Liquid Extraction (B. F. Ruth, A. Loeffler)

The objective of this research is to establish, if possible, the mechanism of the countercurrent movement of the liquid droplets and continuous fluid medium in a spray droplet extraction tower. If successful, it should be possible to predict the amount of

surface area available for mass transfer under all conditions of operation. The ability to predict surface area is essential to both the interpretation of experimental behavior and subsequent design and operation. The present research was suggested by inability to explain the relation between solvent holdup and fluid velocities in the six-inch spray column **extractor** previously tested.¹⁰

Since the mechanism of fluidization of solid spheres by upward streaming liquid would appear to be very nearly the same as that producing "holdup" in a spray column extractor, the theoretical work during the period of this report has been devoted to an attempt to establish the mechanism of fluidization of solids. Although experimental confirmation and testing are still in progress, it appears that we have arrived at a successful and correct mechanism.

The experimental work has consisted of continuation of work described in previous reports interspersed with various short experiments designed to shed light upon questions arising during the development of the theory. These have been:

(1) A study of the fluidization of fluid droplets in a manner analogous to the fluidization of solids.

(2) A study of the effect of tube diameter on the rising velocity of fluid droplets and the fall of solid spheres.

(3) A study of the effect of velocity of the continuous phase on the velocity of rise of liquid droplets.

(4) A study of the factors affecting uniformity of drop size in the formation of the droplets utilized in (1).

(5) A study of the fluidization of glass spheres of sizes 0.0816 cm. down to 0.0207 cm.

(6) A study of the effect of changes in interfacial surface tension on the degree of sphericity maintained by liquid droplets while rising through a quiescent or moving fluid medium.

¹⁰ISC-96

5. Recovery of Spent Silica Gel from the Adsorption Separation of Hafnium and Zirconium (W. R. Millard, R. H. Maitland)

During this period a successful continuous column run was made in which 150 pounds of reactivated silica gel was used. Thirty-four gallons of product solution were obtained; the product zirconium contained 180 ppm of hafnium.

Two stripping tests were performed on 89- and 86-pound batches of spent silica gel. These tests demonstrated that the spent gel can be batch-stripped using the methods previously developed on a laboratory scale. No handling difficulties were encountered, and stripped gels containing 0.1-0.2 per cent zirconium and hafnium oxides were produced.

An investigation has been started to determine the relations between gel moisture content, heat of wetting, and adsorptive capacity for separating hafnium from zirconium. Work to date shows that unsintered silica gel has a maximum heat of wetting with water of 33.4 cal/g at a 3.7 per cent moisture content. Preliminary batch contacts with column feed indicate that this moisture content produces maximum hafnium-zirconium separation, although lower moisture content gel may adsorb more total oxides. The present data are too meager to permit definite conclusions, and additional tests are in progress.

Future column runs are planned using stripped, reactivated gel to fully demonstrate the effectiveness of reclaimed gel and to determine potential gel life.

6. Production of Zirconium by Solvent Extraction (G. H. Beyer, W. R. Millard, R. P. Cox, R. Masteller, M. E. Oldweiler, H. C. Peterson)

A seven-stage mixer-settler unit was constructed and operated during this period for the separation of zirconium from hafnium with a tributyl phosphate-dibutyl ether solvent. The mixer-settler was modeled after the pump-mixer type developed by Knolls Atomic Power Laboratory (KAPL-109,130,513,556). Two runs were made; the second was made with a modified baffle arrangement and gave a zirconium product containing less than 500 ppm hafnium, and raffinate containing 76 per cent hafnium (based on hafnium plus zirconium). This corresponds to better than 99 per cent yield of purified zirconium. The mixer-settler was constructed of plywood and painted with Saran-Cote. This construction did not withstand the solvent, but enough data were obtained to permit building an efficient extractor from resistant material.

Recent extraction runs have been made using a feed made from crude zirconium tetrachloride. It has been demonstrated that this feed extracts as satisfactorily as did the recrystallized zirconyl chloride previously used.

Two extraction runs, one using fresh solvent and the other using regenerated solvent, were made under otherwise identical conditions. The regenerated solvent compared very favorably in all respects with the fresh solvent. Zirconium containing less than 170 ppm hafnium and 95 per cent hafnium were obtained. It was also found that 7N sulfuric acid removes a large proportion of the solids left in the solvent after water-stripping, and sulfuric acid strips plus water washes have been incorporated into the solvent regeneration treatment prior to caustic treatment.

Solvent stripping has been essentially complete when using an 11-stage Scheibel column, but tests using a 15-foot, 2-inch diameter column packed with 3/8-inch Raschig rings did not give complete zirconium removal. A H.E.T.S. of 12 feet was found for the packed column. Stripping tests using a five-stage mixer-settler show complete stripping in only two stages at a water-solvent ratio of 0.8; essentially complete stripping can be obtained in five stages at water-solvent ratios as low as 0.2.

Preliminary investigations on acid recovery from the aqueous streams indicate that good acid recovery may be obtained. The recovery investigation is in the early stages, and a complete method for recovery has not yet been devised. A major effort will be concentrated on this area in future work.

7. Properties of Slurry Reactor Fuel (W. R. Millard, P. R. Crowley, F. M. Jacobsen)

It was found that the fine particle uranium oxide produced by successive hydriding and oxidizing uranium to produce an average particle size of about 2μ had a tendency to agglomerate in water. This agglomeration was observed visually, and sedimentation studies showed the average particle size in water slurries to be 26μ . A slurry made up in a sodium hydroxide monopotassium phosphate buffer was found to contain 53.8 per cent of the oxide as particles smaller than 6.5μ . A slurry was made by dispersing the oxide in a dilute sodium hydroxide solution (pH = 9.6) by circulating the slurry through a colloid mill with 0.0025-inch clearance for 10 minutes. This slurry contained 63.8 per cent of the oxide as particles less than 1.3μ diameter and was very slow in settling. It was noted that all three slurry types changed pH with time, indicating a reaction with the uranium oxide.

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Viscosities of slurries in NaOH solutions have been determined using a Brookfield viscometer in the range of 0.27 to 5.06 per cent oxides. At 35°C the viscosities varied from 0.855 to 0.872 centipoises, as compared to 0.721 for water at 35°C.

An apparatus has been designed and built for continuously measuring slurry densities and from the densities deriving sedimentation rates. A 1.39 per cent oxide slurry in NaOH solution made up as before was found to have a sedimentation rate expressed by $W = 22.92 + 9.37 \ln t$, where W is the weight fraction settled out in t hours.

It is planned to develop a method for continuous production of fine particle oxides, and equipment for this production is being constructed. The chemical and physical stability of the resulting slurries will be studied at elevated temperatures and pressures.

Ceramic Engineering Group

Assembly of apparatus for thermal conductivity measurements has been delayed by space requirements. This assembly will now be undertaken and preliminary tests will be carried out to determine operating efficiency of the apparatus, including maximum temperature, temperature control, and thermal equilibrium characteristics.

Due to a change in body composition of the synchrotron "donut", necessitated by depletion of the original source of material, shrinkage problems have been encountered in the production of the electrical porcelain. A study of the shrinkage factors has been made and will be applied in the design of new molds.

Further study on the thermal properties of refractory materials is planned. This study will also include work on the forming methods of the refractory specimens.

Engineering Development Group

1. Slurry Program

1.1 Literature Survey

A survey of literature on the static and dynamic properties of slurries is substantially complete. It is planned to prepare a report giving a list of references on this subject covering the period 1930-1950.

1.2 Analysis

A number of aspects of the slurry transportation problem have been considered. A purely analytical solution does not appear feasible at this time. Most rapid progress can be made by combining the analytical and experimental approaches.

1.3 Experimental

Equipment for the experimental phase of the slurry program is being assembled. Most of the equipment for the first series of experiments has been completed and the remainder is under construction.

2. MTA Program

Work on this program is reported separately in special monthly reports to UCRL.

3. Summary of Tests

A program is under way for making tension, creep, fatigue, impact and hardness tests on commercial thorium. The tension tests include the evaluation of the modulus of elasticity and the yield strength.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-105 "Kinetics of the Reaction of Uranium with H_2 , HD and D_2 " by H. J. Svec and F. R. Duke. Thesis. UNCLASSIFIED.²
- ISC-143 "Conductances, Transference Numbers, and Activity Coefficients of Chlorides of Some High Atomic Number Rare Earths in Aqueous Solution" by F. H. Spedding and James M. Wright. Thesis. UNCLASSIFIED.
- ISC-145 "A Technique for Producing Fine Particle Thorium Oxide and Uranium Oxide" by Robert S. Hansen and Robert E. Minturn. SECRET.
- ISC-146 "Zirconium Ions in Aqueous Solution" by E. H. Dewell and A. F. Voigt. Thesis. UNCLASSIFIED.
- ISC-147 "Semi-Annual Progress Report in Chemistry for the Period October 1, 1950--March 31, 1951" by F. H. Spedding et. al. SECRET.
- ISC-150 "Optical Properties of Counting Diamonds" by R. K. Willardson and G. C. Danielson. UNCLASSIFIED.
- ISC-151 "Sublimation of Zirconium Tetrafluoride" by Louis J. Abate and H. A. Wilhelm. Thesis. UNCLASSIFIED.
- ISC-154 "Short-Lived Synchrotron-Induced Radioactivities" by F. I. Boley and D. J. Zaffarano. Thesis. UNCLASSIFIED.
- ISC-155 "An Apparatus for Counter Current Liquid-Liquid Solvent Extraction". by H. A. Wilhelm. SECRET.
- ISC-156 "The Oxidation of Stannate(II) Ion by Some Cobalt(III) Complexes" by Richard C. Pinkerton and Frederick R. Duke. UNCLASSIFIED.
- ISC-157 "The Beta-Spectra of p^{32} and p^{33} " by E. N. Jensen, R. T. Nichols, J. Clement and A. Pohm. UNCLASSIFIED.
- ISC-158 "Some Synchrotron-Produced Radioactivities of Tantalum" by Alfred J. Moses and Don S. Martin, Jr. Thesis. UNCLASSIFIED.

- ISC-159 "Transition Probabilities II. Semi-Theoretical f-numbers for Hydrogen Using the Dipole Velocity Operator" by Harrison Shull. UNCLASSIFIED.
- ISC-160 "Electron Deficient Compounds (VI) The Structure of Beryllium Chloride" by R. E. Rundle and Paul H. Lewis. UNCLASSIFIED.
- ISC-162 "Transition Probabilities III. Dipole Velocity Computations for C_2 and N_2^+ . The Question of Degree of Hybridization" by Harrison Shull. UNCLASSIFIED.
- ISC-163 "Characteristics of a Diamond Conduction Counter" by Robert K. Willardson and G. C. Danielson. Thesis. UNCLASSIFIED.
- ISC-164 "Zinc-1,10-Phenanthroline Complexes and Their Analytical Application" by John H. McClure and C. V. Banks. Thesis. UNCLASSIFIED.
- ISC-165 "Spectrophotometric Determination of Cerium" by Richard E. Edwards, A. S. Ayers and C. V. Banks. UNCLASSIFIED
- ISC-170 "Production of Pure Thorium and Uranium Compounds by the Acid Dissolution of Monazite Sand" by G. L. Bridger, et.al. SECRET.
- ISC-171 "Quarterly Summary Research Report for the Period April 1 - June 30, 1951" by W. E. Dreeszen. SECRET.

2. Papers Published in Scientific Journals

Banks, Charles V., and James H. Patterson. "A Polarographic Investigation of Iron-Sulfosalicylate Complex Ions." J. Am. Chem. Soc. 73, 3062-3064 (1951).

Chiotti, P., and B. A. Rogers. "The Production of Uranium and Thorium in the Powder Form." Metal Progress 60, 60-65 Sept. (1951).

Duke, Frederick R., and Robert F. Bremer. "A Kinetic Study of the Periodate Ion and the Periodate-Glycol Complex." Iowa State Coll. J. Sci. 25, 527-529 (1951).

Duke, Frederick R., and Richard C. Pinkerton. "The Role of Halide Ions in the Ferric-Stannous Reaction." J. Am. Chem. Soc. 73, 3045-3049 (1951).

Godycki, L. Edward, R. E. Rundle, Roger C. Voter, and Charles V. Banks. "Possible Existence of a Symmetrical O...H...O Hydrogen Bond in Nickel Dimethylglyoxime." J. Chem. Phys. 19, 1205-1206 (1951).

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Leachman, R. B. "On the Ionization Yields of Fission Fragments." Phys. Rev. 83, 17-20 (1951).

Meek, H. V., and Charles V. Banks. "Composition and Stability of the Beryllium-Sulphosalicylate Complex Ion." J. Am. Chem. Soc. 73, 4108-4112 (1951).

Rundle, R. E. "The Hydrogen Positions in Uranium Hydride by Neutron Diffraction." J. Am. Chem. Soc. 73, 4172-4174 (1951).

Shull, Harrison, and Frank O. Ellison. "The Effect of Variation of Z upon the Theoretically Computed Energy Levels of Benzene." J. Chem. Phys. 19, 1215-1216 (1951).

Snow, A. I., and R. E. Rundle. "The Structure of Dimethylberyllium." Acta Cryst. 4, 348-352 (1951).

Thamer, B. J., and A. F. Voigt. "Zirconium Chloranilate Complexes." J. Am. Chem. Soc. 73, 3197-3202 (1951).