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A STUDY OF THE EMANATION METHOD FOR THE DETERMINATION
OF THE SURFACE AREA OF THORIUM OXIDE

by

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
1. INTRODUCTION	5
2. SAMPLE PREPARATION	7
3. PROPORTIONAL COUNTER	7
4. OPERATING CHARACTERISTICS OF THE SYSTEM	10
5. THEORY OF THE EMANATION PROCESS	12
6. RECOIL RANGE OF Rn^{220}	15
7. DETERMINATION OF RECOIL EMANATION BY α COUNTING .	16
8. EMANATION MEASUREMENTS	17
9. SUMMARY	23
APPENDICES	
A. The BET Low-temperature Absorption Method for Determining Surface Areas	26
B. Derivation of the Expression for E_R	27
C. Calculation of Recoil Range of Rn^{220}	29
D. Background Study	30
BIBLIOGRAPHY	31

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Change in E_R and Surface Area as a Function of Firing Temperature	18
2	Change in E_R and Surface Area as a Function of Firing Time at 500°C	20
3	Change in E_R and Surface Area as a Function of Firing Time at 900°C	21
4	Change in E_R and Surface Area of $\text{ThO}_2\text{-UO}_2$ as a Function of Firing Temperature	22
5	Net Counting Rate after Correcting for Deposited Background	30

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Spherical Particles of Thorium Oxide-Uranium Oxide Fired for 1 Hr at 650°C	8
2	Cylindrical Geometry Proportional Spectrometer	9
3	Block Diagram of Electronic Circuit, Counter, and Sampling System	9
4	Thoron Decay Scheme and Alpha Energies	10
5	Typical Emanation Spectrum from Thorium Oxide	10
6	Count Rate as a Function of Gas Flow	12
7	Thorium or 4n Series	14
8	Thoron Activity at Time t after Thorium Separation	15
9	Alpha Spectrum of Deposited Background Activity	17
10	Change of Recoil Emanation from Thorium Oxide as a Function of Firing Temperature	19
11	Change in Density as a Function of Firing Temperature	19
12	Surface Area Change as a Function of Firing Temperature	19
13	Change in Surface Area as a Function of Firing Time at 500°C	21
14	Change in Surface Area as a Function of Firing Time at 900°C	22
15	Surface Area Change as a Function of Firing Temperature for ThO ₂ -UO ₂ System	23
16	Recoil from a Spherical Surface where $r \gg R$	27
17	Correction for Variable Background Activity Deposited in Counter	30

A STUDY OF THE EMANATION METHOD FOR THE DETERMINATION OF THE SURFACE AREA OF THORIUM OXIDE

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ABSTRACT

The surface areas of several thorium oxide and thorium oxide-uranium oxide preparations were measured by the emanation method. The radioactive gas-counting system employed is described, and a discussion of the procedure for converting counting data to terms of emanating power and finally to surface area values is given. Surface area values by the emanation method are compared with BET values from like samples. The difference between values obtained by the two methods is attributed to the efficiency of the radioactive gas-detecting system and the porosity of the oxide samples. The contribution of Rn^{222} from the oxide samples containing uranium was found to be negligible and presented no problem. Samples fired at temperatures above 1500°C for one hour in air exhibited a marked increase in "room temperature" emanation rates. The predicted lattice-loosening temperature of metal oxides is approximately one-half their absolute melting point. Above this temperature, sufficient thermal agitation is induced to permit exchange and possibly permanent displacement of atoms in the crystal lattice.

Therefore, firing these oxide preparations at temperatures above 1500°C probably results in lattice defects throughout the crystal structure, with the surface defects contributing to an increase in surface area and a corresponding increase in the emanation rate.

1. INTRODUCTION

The use of an aqueous slurry of thorium oxide-uranium oxide as circulating fuel in thermal breeder reactor has long been recognized as an interesting possibility. There are many predicted advantages to a system of this type. On the other hand, however, many questions arise in connection with the feasibility of using a particular type of slurry material as the circulating fuel. These questions usually pertain to such properties as

settling characteristics, flocculation, particle shape, particle size, absorption characteristics of the slurry material, corrosion-erosion effects, fission product release, and thermal and radiation stability of the slurry material. To obtain a useful understanding of any one of the above-mentioned characteristics it is very essential that certain common physical properties of the slurry material be known. One of these properties, which usually requires several hours for a single determination, is surface area.

The purpose of the work covered in this report was to evaluate a modified emanation method for determining surface areas of thorium oxide and thorium oxide-uranium oxide preparations.

The emanation method differs from other known methods in that a complete alpha-particle spectrum of the emanation (Rn^{220}) and its daughter products can be observed, thus enabling precise background or "deposited activity" corrections to be made. The results of this study were then used in an attempt to obtain some relation between emanating power and its changes and specific surface and its changes.

The samples used in this study were powders of thorium oxide and some mixtures composed of thorium oxide-uranium oxide with the uranium content being $\sim 10\%$ by mass.

The first series of samples consisted of thorium oxide preparations fired for the same period of time at different temperatures ranging from 225°C to 900°C . Then, measurements of surface area of these samples were made by the emanation technique. These values were compared with those obtained by using the Braunaur, Emmett and Teller (BET) method (see Appendix A). It was found that in each case the surface value by the emanation technique was less than the value obtained by the BET method. Also, it was found that the deviation between the values obtained by the two methods decreased with increasing firing temperature.

With a further increase in firing temperature, the two values approached one another and differed by a very small value.

The second and third series of samples, also of thorium oxide, were fired at given temperatures, 500° and 900°C , with the period of firing varied up to sixty-four hours. Again, measurements of surface area were made by the emanation technique and compared with those obtained by the BET method. In these cases it was found that large reductions of surface area took place during the short heating periods up to about seven hours. Longer heating periods, up to sixty-four hours, produced only slight additional decrease in surface area. In these cases, the values of the surface areas obtained by the two methods differed from each other by a constant multiplicative factor.

The fourth series consisted of samples of a thorium oxide-uranium oxide mixture. These were each fired at different temperatures for the same length of time and their surface areas measured by the two methods. The presence of Rn^{222} (with a half-life of 3.82 d) presented no problems in connection with the alpha counting. The samples fired above 1450°C showed an increase in surface area, as determined by the emanation method. This apparent increase is in agreement with the "lattice loosening theory" of Tammann.⁽¹⁾

2. SAMPLE PREPARATION

Since the material under investigation was thorium oxide, there was no doubt as to homogeneous distribution of the parent of the radioactive inert gas. Both thorium nuclides (Th^{232} and Th^{228}) of which the oxide is formed furnish ThX by natural decay. This conveniently eliminates the problem of incorporating an active parent in the material by the usual method of coprecipitation.

The problem of the geometry of the particles was simplified by the method used for their preparation.⁽²⁾ A nitrate-stabilized thoria sol was atomized in a column of gaseous anhydrous ammonia. The resulting material was collected from the bottom of the column, washed with 6-8 normal ammonium hydroxide, then with methyl alcohol, and then fired.

An electric furnace equipped with a temperature controller was used for the firing. The furnace was slowly brought up to the prescribed temperature, held at this temperature for a given period of time, and then turned off. After the furnace had cooled to room temperature, the sample or samples were removed, transferred to a weighing bottle, and stored in a desiccator.

Examination of the material produced in this manner has shown that only about 2% is nonspherical (see Fig. 1).

All material for this experiment was screened, and the fraction passing through a NBS No. 100 sieve and retained on a No. 325 sieve was used.

3. PROPORTIONAL COUNTER

Figure 2 shows a perspective drawing of the detector used for the continuous flow measurements of thoron. Detailed information on its construction is given by Gatrousis and Crouthamel.⁽³⁾ The only modification was the use of a one-mil instead of a 2-mil center wire, permitting the counter to be operated at a lower voltage (850 volts). A modified (Los Alamos model 100) pre-amplifier was connected directly to one of the Lucite end blocks of the counter. The output from the pre-amplifier was

passed to an (Argonne type A-61) linear amplifier and then to a 256-channel analyzer. Figure 3 is a block diagram of the electronic circuits, counter, and sampling system.

FIG. 1
SPHERICAL PARTICLES OF THORIUM OXIDE-URANIUM OXIDE
FIRED FOR 1 hr AT 650 °C

Operation of the counter was as follows: The counting gas mixture (P-10), 90% argon and 10% methane, was supplied from a commercial gas cylinder at a constant, predetermined flow rate. As the gas passed over the thorium oxide and out of the sample chamber, it carried with it the emanation (Rn^{220}) from the thorium oxide, which then went directly into the counter. The alpha particles resulting from the decay of thoron in the counter expended their energy by ionization of the counting gas. In the 90% argon-10% methane mixture, about 30 ev of energy are spent per ion pair formed. The operating voltage of the counter was below the proportional region and no multiplication near the center wire occurred.

The counter thus operated as an ionization detector. However, the number of ion pairs formed by a given alpha particle, and consequently the size of the pulse fed to the 256-channel analyzer, was proportional to its energy.

FIG. 2
CYLINDRICAL GEOMETRY PROPORTIONAL SPECTROMETER

FIG. 3
BLOCK DIAGRAM OF ELECTRONIC CIRCUIT, COUNTER, AND SAMPLING SYSTEM

Examination of the thoron decay scheme (see Fig. 4) shows that several of the daughters also decay by alpha emission. These daughter products are not gaseous and contribute to the so-called "deposited background" of the counting chamber. A method of correcting for this activity will be discussed later.

Figure 5 shows a trace of a typical alpha spectrum obtained with the counting system discussed above. The trace of this spectrum is also evidence of the relatively modest but very useful resolution (3-4%) that can be obtained with the simple and inexpensive alpha spectrometer used in this work.

FIG. 4
THORON DECAY SCHEME AND ALPHA ENERGIES

FIG. 5
TYPICAL EMANATION SPECTRUM FROM
THORIUM OXIDE

4. OPERATING CHARACTERISTICS OF THE SYSTEM

Statistical considerations make it desirable to observe the maximum number of counts per unit of time from any given sample. In this system the counting rate is a function of the flow rate of the argon-methane mixture. An excessively high flow rate will have a dilution effect on the thoron and will also transport a large fraction of it through the counter before decay occurs. An excessively low flow rate will permit a larger fraction of decay to occur before the thoron has reached the effective counting zone.

In order to estimate what flow rate should be employed, the results of W. B. Silker⁽⁴⁾ were used. He has shown that the theoretical flow rate for obtaining maximum thoron decay in a counter in a continuous flow system can be calculated in the following manner. Assuming linear flow in the system, V_1 and V_2 being the volume of the sample chamber and the counter, respectively, and substituting volume flow rate for time, the equation he employed is given as:

$$N = N_0 \left(e^{-\lambda V_1/F} - e^{-\lambda(V_1 + V_2)/F} \right), \quad (1)$$

where

N = the number of thoron atoms decaying in V_2 ,

N_0 = the number of thoron atoms initially present,

λ = the decay constant for thoron (in reciprocal minutes), and

F = the flow rate (in $\text{cm}^3/\text{minute}$).

Then, in order to determine the flow rate for maximum thoron decay, the following equation is solved for F :

$$\frac{dN}{dF} = N_0 \left[\frac{\lambda V_1}{F^2} e^{-\lambda V_1/F} - \frac{\lambda(V_1 + V_2)}{F^2} e^{-\lambda(V_1 + V_2)/F} \right] = 0 \quad (2)$$

It was found that

$$F = \frac{\lambda V_2}{\ln [1 + (V_2/V_1)]} \quad (3)$$

Equation (3) gave, for the apparatus used, a numerical flow rate of 396 cc/min as against the experimentally determined value of 235 cc/min. Figure 6 is a plot of the experimentally determined counting rates observed at various intervals of increasing flow of gas through the counter.

The same discrepancy between the calculated and experimental values has been observed by Silker⁽⁴⁾ and was attributed to incomplete mixing of the gas stream in the counter.

From Fig. 3 it can be seen that, when the system is opened to introduce a sample, the counter can be isolated from the rest of the system to prevent air from entering the counter. After the sample is in place, the sample chamber is closed, vented, and flushed with counting gas for about 5 minutes to sweep out the air. Then the vent is closed and the other valves are adjusted to permit the flow of gas leaving the sample chamber to enter the counter. Eight minutes of flow were required for the radon-bearing gas to come to equilibrium in the counter.

FIG. 6
COUNT RATE AS A FUNCTION OF GAS FLOW

Although the design of the sample chamber is relatively simple, a few comments about it are in order at this point. At the beginning of this work, a chamber having one gas inlet and one outlet port was used. The outlet port was located in the center of the chamber cover and the sample planchet positioned on the base plate directly beneath this port. The single inlet port was located in the base plate about one inch from the circular area covered by the planchet. With this design, it was noted that a sample counted several times, under the same conditions except for its position in the chamber with respect to the gas inlet and outlet ports, gave a variety of counting rates.

It was assumed that this problem was due to incomplete mixing of the gases and correction was made by redesigning and building a new chamber. The new design entailed reducing the volume of chamber and inserting a total of four inlet ports and nine outlet ports in positions in the chamber to provide the necessary turbulent flow. With this design, reproducible counting rates were obtained from a given sample irrespective of its position in the chamber.

5. THEORY OF THE EMANATION PROCESS

The theory of the emanation process is given in considerable detail in the publications of Flüge and Zimmens⁽⁵⁾ and Zimmens^(6,7,8). The following discussion covers only those theoretical details which are significant to this particular study.

Emanating power E has been defined as the fraction of radioactive inert-gas atoms formed in a solid that escape from the solid. Zimmens⁽⁶⁾ has shown that the inert-gas atom may escape from the solid either by recoil or by diffusion, so that

$$E = E_R + E_D \quad (4)$$

If one is able to resolve these two factors, then it is possible to calculate the surface area of the solid by the use of the following relationship:

$$E_R = \frac{3}{4} \left(\frac{R}{r_0} \right) - \frac{1}{16} \left(\frac{R}{r_0} \right)^3, \quad (5)$$

where

R = the recoil range, and

r_0 = the radius of the particles.

For spherical particles, for which $r_0 \gg R$, equation (5) reduces to

$$E_R = \frac{R}{4} \rho \left(\frac{\text{surface}}{\text{mass}} \right) \quad (6)$$

The derivation of this relationship is given in Appendix B. In this study all emanation measurements were made at room temperature, and the temperature-dependent diffusion effect (E_D) was considered negligible.

One of the limiting factors in the interpretation of the emanation data obtained in this work was the determination of the rate of formation of the inert-gas atoms in the solid. The continuous flow of counting gas across the sample as used in this study, unlike the Hahn⁽⁹⁾ technique, does not lend itself to the measurement of the emanating power directly. Therefore, the rate of formation of the inert-gas atoms had to be found by some other means, since only the rate of escape of thoron could be accurately determined by alpha counting.

From the decay scheme of Th^{232} shown in Fig. 7, it is apparent that when thorium is separated from monazite or thorite the two isotopes, Th^{232} and Th^{228} are obtained. Except for cases where extreme purity is desired, the thorium at this point is essentially "daughter free."

If the separation time of the thorium is known, that is, the time when secular equilibrium is destroyed by the separation of Th^{232} and Th^{228} from their daughter products, then the rate of formation of the inert-gas atoms can be calculated. By employing the Bateman⁽¹⁰⁾ equation

$$N = A_0 (h_A e^{-\lambda_A t} + h_B e^{-\lambda_B t} + h_C e^{-\lambda_C t}) \quad (7)$$

where A_0 is the number of Th^{232} atoms initially present and λ_A , λ_B , and λ_C are the decay constants of Th^{232} , Ra^{228} , and Th^{228} , respectively, and the dimensionless functions of the decay constants have the following systematic form:

$$\begin{aligned} h_A &= \frac{\lambda_A}{\lambda_C - \lambda_A} \frac{\lambda_B}{\lambda_B - \lambda_A} \\ h_B &= \frac{\lambda_A}{\lambda_A - \lambda_B} \frac{\lambda_B}{\lambda_C - \lambda_B} \\ h_C &= \frac{\lambda_A}{\lambda_A - \lambda_C} \frac{\lambda_B}{\lambda_B - \lambda_C} \end{aligned} \quad (8)$$

the thoron activity, due to buildup from Th^{232} , can be calculated for any time t after separation. Likewise, the thoron activity due to the natural decay of Th^{228} at any time t after separation can be calculated after a value for N at t_0 has been determined, in which N represents the number of Th^{228} atoms initially present at time of separation.

FIG. 7
THORIUM OR $4n$ SERIES

Figure 8 is a plot of the change in thoron activity with time. The calculated values are based on one gram of daughter-free thorium having the natural ratio of Th^{232} to Th^{228} at time t_0 . It should be noted that the thoron activity reaches a minimum value at approximately 4.5 years after the thorium separation, then increases to approach the secular equilibrium value as an asymptote. An approximate value for thoron decay can be obtained by taking the sum of the two points on the curves at any time t after separation.

FIG. 8
THORON ACTIVITY AT TIME t AFTER THORIUM SEPARATION

6. RECOIL RANGE OF Rn^{220}

The atomic stopping power of a substance is generally assumed to be the same for recoil atoms as for alpha particles. Then, by employing the values of Livingston and Bethe⁽¹¹⁾ and applying the appropriate correction factors for density, atomic or molecular stopping power, and so on, the recoil ranges in different materials can be calculated. For example, a range in thorium oxide, R_{ThO_2} , is given in terms of the range in air:

$$R_{\text{ThO}_2} = R_{\text{air}} \frac{\rho_{\text{air}}}{\rho_{\text{ThO}_2}} \sqrt{\frac{A_{\text{ThO}_2}}{A_{\text{air}}}}, \quad (9)$$

where A_{air} is the "atomic weight of air," that is, the square of the weighted average square root value: $(0.8\sqrt{14} + 0.2\sqrt{16})^2 = 14.4$. The value of A for compounds and mixtures are handled in the same way.

Flügge and Zimmens⁽⁵⁾ estimated the recoil range of thoron by employing the expression

$$R = G \frac{1}{\rho} \left(\frac{\overline{AW}}{s} \right) \quad , \quad (10)$$

where G is a proportionality constant, ρ is the density of the solid, and $(\overline{AW}/s)$ is the average ratio of the atomic weight to the atomic stopping power, relative to air, of the atoms in the solid. Either of these methods may be used to calculate the range of recoil emanation in lieu of the lacking experimental measurements.

In this study Eq. (9) was employed. If R in Eq. (6) is replaced with the expression for R_{ThO_2} given in Eq. (9), then the equation for surface area reduces to

$$\text{Surface} = \frac{4E_R(\text{mass})}{R^1} \quad , \quad (11)$$

where R^1 is the "recoil range factor" for thoron in ThO_2 and equal to

$$R^1 = R_{\text{air}} \rho_{\text{air}} \sqrt{\frac{A_{\text{ThO}_2}}{A_{\text{air}}}} = R_{\text{ThO}_2} \rho_{\text{ThO}_2} \quad . \quad (12)$$

Further discussion of recoil range is given in Appendix C.

7. DETERMINATION OF RECOIL EMANATION BY α COUNTING

The decays of Rn^{220} and of its daughter products include four nuclides that involve alpha emission: Rn^{220} , Po^{216} , Bi^{212} , and Po^{212} . During the normal operation of the counter Pb^{212} , from the decay of Po^{216} , becomes deposited on the inner surface of the counting chamber. This deposited material decays by beta emission, with a 10.6-hr half-life, to Bi^{212} and finally to Po^{212} , both of which are alpha emitters. If the counting is started in a relatively clean counter, the "deposited background" will remain practically negligible for several hours. However, even a low background may represent an appreciable percentage of the total activity when the emanation from a particular sample is low. Therefore the following method was employed for making background corrections for all emanation measurements made in this study.

Let it be assumed that the counter has been in constant use for several days and that there is a considerable amount of deposited activity present in the counter. The counting gas is diverted to bypass the sample chamber and pass only through the counter, with the gas flow rate and all other operating conditions maintained constant. A measurement is made

of the deposited activity, and the peak-to-total ratio for Po^{212} is determined over a given energy span. The energy span from 5.5 to 9.0 Mev, that was observed was chosen to include the energies of the Rn^{220} , Po^{216} , Bi^{212} , and Po^{212} . Figure 9 shows a typical spectrum from "deposited background" activity only. Several determinations of the peak-to-total ratio gave values that agreed within ± 4 per cent. The background correction is then made by determining the counts under the Po^{212} peak (8.77 Mev) obtained from the composite alpha spectrum from a sample. These counts are then converted to background activity by dividing by the peak-to-total ratio. This background is subtracted from the counts, totaled over the same energy span, i.e., 5.5 to 9.0 Mev, that were obtained from the sample. It should be noted that the total activity minus background activity represents the activity due to both Rn^{220} and Po^{216} and must be taken into consideration when calculating E_R . The results of eight ten-minute counts collected at intervals over a six-hour period, while active gas was continuously flowing through the counter, are shown in Appendix D.

FIG. 9
ALPHA SPECTRUM OF DEPOSITED
BACKGROUND ACTIVITY

8. EMANATION MEASUREMENTS

The first set of measurements was made on a group of ThO_2 samples fired at temperatures ranging from 225°C to 900°C for a period of two and one-half hours. A small (approximately 200 mg) portion of each sample was weighed out and used for the determination.

In Table 1 are shown the specific surface values obtained from the emanation measurements employing Eq. 11. The relationship between these values and the absolute surface area values obtained by the BET method will be discussed later.

Table 1

CHANGE IN E_R AND SURFACE AREA AS A
FUNCTION OF FIRING TEMPERATURE

Firing Temp, °C	E_R , Per Cent	Surface Area, m ² /gm
225	10.2	1.1
350	6.8	0.74
500	4.6	0.50
650	2.1	0.22
650	2.0	0.21
650	2.2	0.23
900	0.080	0.0085
900	0.076	0.0082

Figure 10 is a semilogarithmic plot of the data in Table 1. Between 225°C and 650°C the emanating power E_R can be determined from the equation

$$E_R = 18.32 e^{-0.031x} \quad , \quad (13)$$

where x is the firing temperature (°C). Above 650°C the "room temperature curve" drops sharply and at 900°C reaches 0.08 per cent.

The comparatively high emanating power value of the 225°C-fired sample is indicative of the tremendously large surface areas developed in thorium oxide "hydrogels."

The curve shown in Fig. 11 was plotted from the firing temperature versus the pycnometric density data of Foex.⁽¹²⁾ These data show that a considerable change of surface area can be expected with firing, up to temperatures of about 900° to 1000°C.

Figure 12 is a plot of the firing temperature versus specific surface area (m²/gm) showing the relationship between the surface values obtained by both the emanation and BET methods. The curves clearly show that the two methods are not equally sensitive to the surface changes occurring over the firing temperature range from 250°C to 900°C. As the firing temperatures increase, the BET method detects a progressively greater decrease

of surface area than the emanation method. In the vicinity of 900°C , the difference between the two values of surface area appears to be approaching a minimum value.

FIG. 10
CHANGE OF RECOIL EMANATION FROM THORIUM OXIDE
AS A FUNCTION OF FIRING TEMPERATURE

The following argument is offered as a plausible explanation of this interesting phenomenon. With each firing at a higher temperature, shrinkage and structural changes begin to have a pronounced effect on the porosity of the amorphous thorium oxide particles. The surfaces of extremely small deep pores, which served as adsorption sites for BET measurements, are now either greatly reduced or completely eliminated at the higher firing temperatures.

FIG. 11
CHANGE IN DENSITY AS A FUNCTION OF FIRING
TEMPERATURE. (FIRING TIME - 1 hr)

FIG. 12
SURFACE AREA CHANGE AS A FUNCTION OF
FIRING TEMPERATURE. (TIME AT HEAT = 2.5 hr)

The decrease in porosity has only a small effect on the emanation measurement. This is understandable because the emanation method does not detect the tremendous internal surface of the porous particles. However, a reduction in that fraction of the total porosity which is present in the outer or skin of the particle results in a smaller surface area change, which the emanation method does detect.

Therefore, over the firing temperature range from 250° to 900°C, in which internal porosity is being eliminated or reduced to the point where the BET adsorbate cannot reach the adsorption site, a larger decrease in surface area can be expected to be measured by the BET method than by the emanation method.

A second series of measurements was made to determine the effect of firing time on the change in surface area. A firing temperature of 500°C was selected because it was just below the temperature range where the most pronounced surface changes occurred. Therefore, it was expected that prolonged heating at this lower temperature, 500°C, would produce the same surface changes as a shorter firing at a higher temperature. However, the data from this series of measurements show that very little surface area change occurs after the initial 2.5-hour firing period. This holds true for firing times up to 64 hours, as shown in Table 2.

Table 2
CHANGE IN E_R AND SURFACE AREA
AS A FUNCTION OF FIRING TIME
AT 500°C

Firing Time, hr	E_R , Per Cent	Surface Area, m^2/gm
2.5	4.5*	0.49
7.5	4.3*	0.47
15.5	4.0*	0.44
44	4.0*	0.44
64	4.4	0.48

*Average of two or more measurements

From an extrapolation of the curves in Fig. 12, the surface area of all the starting material used in the work described in this paper is assumed to be approximately 1.2 m^2/gm and 200 m^2/g . This would be as determined by the emanation method and the BET method, respectively, and prior to any heat treatment.

FIG. 13
CHANGE IN SURFACE AREA AS A FUNCTION OF
FIRING TIME AT 500°C

The emanation values plotted in Fig. 13 are in very good agreement with the BET data in the sense that they differ a uniform constant factor.

The third series of measurements was again a study of the change in surface area with firing time, but at 900°C. The data in Table 3 contain the measurements made up to a firing time of 15 hours. Plots of these data along with some corresponding BET values are shown in Fig. 14. The interesting point to note here is that a considerably longer firing time is required before the point is reached where a negligible decrease in surface area occurs with further firing. At 900°C, the time required to reach the leveling-off point is ~9 hours.

Table 3

CHANGE IN E_R AND SURFACE AREA
AS A FUNCTION OF FIRING TIME
AT 900°C

Firing Time, hr	E_R , Per Cent	Surface Area, m²/gm
2.5	0.080	0.009
7.0	0.016	0.002
15.0	0.011	0.001

A fourth series of samples, consisting of thorium oxide-uranium oxide (10% U), was prepared and fired according to the procedures previously described. The firing time for this series was held to 1 hour and the temperature varied between 650° and 1750°C.

A preliminary examination of this material by alpha counting showed that there was no detectable interfering alpha contribution from Rn^{222} ($t_{1/2} = 3.82$ d).

Because of the lower emanating power of the high-temperature-fired material, the sample size used for counting was increased to about 1 gram. Four-inch diameter aluminum planchets were used so that the

sample thickness on the planchet could be kept to a minimum. The per cent emanation due to recoil (E_R) and the surface area, as calculated by Eq. (11), are given in Table 4. Data are shown in Fig. 15.

FIG. 14
CHANGE IN SURFACE AREA AS A FUNCTION OF
FIRING TIME AT 900°C

Table 4

CHANGE IN E_R AND SURFACE AREA OF
 $\text{ThO}_2\text{-UO}_2$ AS A FUNCTION OF
FIRING TEMPERATURE

Firing Temp, °C	E_R , Per Cent	Surface Area, m^2/g
650	2.0	0.22
1200	0.031	0.0034
1200 (for 2 hrs)	0.019	0.0021
1200 (for 2 hrs)	0.020	0.0022
1400	0.033	0.0036
1600	0.090	0.0096
1750	0.34	0.037
1750	0.34	0.037

From particle size distribution and density data on a thorium oxide-uranium oxide sample fired at 1200°C, the calculated surface area, assuming zero porosity and perfect spheres, was 0.01 m^2/g . An explanation of this apparent discrepancy will be given in Section 9.

FIG. 15
SURFACE AREA CHANGE AS A FUNCTION OF
FIRING TEMPERATURE FOR $\text{ThO}_2 - \text{UO}_2$
SYSTEM. (FIRING TIME: 1 hr)

It may be seen from Table 4 and Fig. 15 that an increase in surface area appears to occur in material fired above 1500°C. At 1750°C, the magnitude of the increase of surface area is certainly beyond the limits of any reasonable probable error that we might assign to the emanation measurements.

9. SUMMARY

1. A study was made of the emanation method for determining the surface area of spherical thorium oxide particles using a cylindrical geometry proportional spectrometer and a continuous-flow counting system to measure the alpha-particle decay of the recoil emanation from various thorium oxide preparations.

2. The data clearly show that direct interpretation of E_R values from the thorium oxide preparations, in terms of surface area, does not result in values that agree with the "absolute" values obtained by the BET method.

3. Agreement can be established between the two methods by applying two correction factors to the emanation surface values. The first factor, C_1 , corrects for the efficiency of the counter and for decay losses occurring in the system before and after the effective volume of the counter.

By applying the following reasoning to the data on the high-fired thorium oxide-uranium oxide preparations, a value for C_1 was obtained. The surface area values, obtained by both the emanation and BET methods, reach a minimum at 1200°C. This would indicate that the porous structure of the preparation was completely destroyed. To verify this, the specific surface area of the 1200°C-fired material was calculated. This calculation was based on particle size distribution data, and perfect nonporous spheres with a density of 9.8 gm/cm³ were assumed. The computation resulted in a specific surface of 0.01 m²/gm, as compared to the 0.03 m²/gm actually found.

Therefore, in the case of this sample fired to 1200°C, both the emanation and BET method detect the same external or geometrical surface. However, the emanation value is less than the BET value by a factor C_1 . In this study C_1 was found to have a numerical value of ~ 8.7 .

The second factor, C_2 , corrects for what might be termed the increasing efficiency of the emanation method that occurs when the porosity of the amorphous oxide is reduced by firing. The value of this factor will be some function of the firing temperature, firing time being constant. It can be obtained from the curves plotted from both emanation and BET data on at least three samples fired over a well-spread temperature range, i.e., 200°C, 600°C, and 1000°C.

It should be made clear that the calibration curves or the expression for C_2 derived from them is only applicable to a particular study, that is, data from preparations fired for two hours at various temperatures cannot be employed in a study where the firing period is to be five hours.

However, once the necessary basic data has been obtained for a particular study then numerous measurements can be made and specific surface values calculated in a fraction of the time required to make a single BET measurement.

4. The increase in surface area occurring at temperatures above 1500°C indicates that emanating power data furnishes a clear index of the temperatures at which reactions in the solid state may be expected to take place. The nature of the physical changes occurring in the material fired above 1500°C that effect a surface increase is uncertain.

5. A large fraction of the increase in surface area of the thoria-urania preparations fired above 1500°C can be accounted for by "lattice loosening." The temperature at which lattice loosening occurs was defined by Tammann⁽¹⁾ as the point of incipient softening. It is apparently the temperature at which reactions in the solid state become operative.

6. The ratio of the lattice loosening or "Tammann temperature" to the melting temperature usually results in values lying between 0.5 and 0.6, if an absolute temperature scale is used. From the emanation data obtained in this study, the lattice loosening temperature of ThO_2 , neglecting the small UO_2 fraction, was found to be 1460°C or 1733°K . Taking the melting point of ThO_2 as 3050°C or 3323°K , there results a ratio of 0.52, which is in good agreement with Tammann's work.

Appendix A

BET LOW-TEMPERATURE ADSORPTION METHOD FOR DETERMINING SURFACE AREAS

Detailed information on the theory and experimental technique of the BET method can be found in a wide variety of text books.^(13,14) However, at this point, a few remarks about the principle of the method will be of value in understanding the interpretation of the data.

The method entails selecting from an experimental adsorption isotherm a point representing the volume and hence the number of molecules corresponding to a monomolecular layer of the adsorbate. Then, multiplication by the average cross-sectional area of each molecule will yield the absolute surface area.

The accuracy of the method rests upon the exactness with which the point corresponding to a monolayer of adsorbed molecules can be picked and the closeness to which one can approximate the average area covered by a molecule of the adsorbate.

Molecular areas corresponding to the packing of molecules in the liquefied adsorbate are in general about 20 per cent larger than those corresponding to the packing of the molecules in the solidified adsorbate. Hence, absolute surface area measurements must be regarded as uncertain by at least this amount.

All BET measurements cited in this paper were made by the Armour Research Foundation. Ethylene was employed as the adsorbate. However, the measurements should be quite comparable to measurements by nitrogen adsorption since the cross section of the adsorbed nitrogen and ethylene molecules are 15.8 and 17.5 square Angstroms, respectively. Thus, the ethylene molecule should be able to penetrate most of the open pores and crevices accessible to the nitrogen molecule. From this we can conclude that the adsorption or BET method can be employed for either porous or nonporous solids, and that the surface area obtained will include the inner surface as well as the outer or geometric surface.

Appendix B

DERIVATION OF THE EXPRESSION FOR E_R

In this derivation it is assumed that the particles are spherical, with a radius $r > 10^{-4}$ cm, and $r \gg R$, where R is the recoil range. Since r is many times greater than R , the illustration shown in Fig. 16 is valid. A Rn^{220} recoil atom can escape from the surface of a particle only if its parent lies within the range R of the surface. Then the fraction of inert-gas atoms (Rn^{220}) formed from parents (Ra^{224}) lying within the range R from the surface is

$$R \frac{\text{surface}}{\text{volume}}$$

$$\frac{\text{AREA OF CONVEX SURFACE OF SECTOR}}{\text{AREA OF SPHERE}} = \frac{2\pi R(R-X)}{4\pi R^2} = \frac{R-X}{2R}$$

$$\int_0^R \frac{R-X}{2R} dX = \frac{1}{4}$$

$$E_R = \frac{R}{4} \left(\frac{\text{SURFACE}}{\text{VOLUME}} \right) = \frac{R}{4} \left(\frac{\text{SURFACE}}{\text{MASS}} \right) \rho$$

ρ = DENSITY

FIG. 16
RECOIL FROM A SPHERICAL SURFACE WHERE $r \gg R$

If we next consider a point P located at some distance X from the surface of the sphere, where X is less than R , as being located between two planes a distance R apart, then each Ra^{224} decay event that occurs at point P will result in a Rn^{220} atom recoil terminating at the surface of a sphere represented by the circle in Fig. 16. The fraction of the Rn^{220} atoms formed at a distance X from the surface that escape by recoil is then

$$\frac{2\pi R(R-X)}{4\pi R^2} = \frac{R-X}{2R}$$

The fraction that escape by recoil over all values of X from 0 to R is given by

$$\frac{\int_0^R \frac{R-X}{2R} dx}{R} = \frac{1}{4} \quad .$$

Thus the emanating power due to recoil is

$$E_R = \frac{R}{4} \left(\frac{\text{surface}}{\text{volume}} \right) = \frac{R}{4} \rho \left(\frac{\text{surface}}{\text{mass}} \right) \quad .$$

Appendix C

CALCULATION OF RECOIL RANGE OF Rn^{220}

The recoil range of Rn^{220} was calculated by employing the expression

$$R_{\text{ThO}_2} = R_{\text{air}} \frac{\rho_{\text{air}}}{\rho_{\text{ThO}_2}} \sqrt{\frac{A_{\text{ThO}_2}}{A_{\text{air}}}} .$$

The value of R_{air} for Rn^{220} was assumed to be the same as that for alpha particles, for namely, 8.3×10^{-3} cm, obtained from M. Livingston and H. Bethe.⁽¹¹⁾ The other values used were:

$$A_{\text{ThO}_2} \text{ --- } 191$$

$$A_{\text{air}} \text{ --- } 14.4$$

$$\rho_{\text{air}} \text{ --- } 1.23 \times 10^{-3} \text{ gm/cm}^3 .$$

For samples fired under different conditions ρ_{ThO_2} takes on a wide range of values. The effect of both firing time and firing temperature on the density of the resulting oxide is thoroughly discussed by M. Foex.⁽¹²⁾ However, in the process of calculating the surface area from Eq. (6), we can obtain a value for $R_{\text{ThO}_2} \rho_{\text{ThO}_2}$ which is designated as R^1 and which leaves Eq. (11) independent of the density of the thorium oxide sample. In the samples containing both ThO_2 and UO_2 the change in recoil range due to the uranium was considered negligible and no correction was made.

Appendix D

BACKGROUND STUDY

A peak-to-total ratio of 0.184 was used in the background study cited here. This value represents the ratio of deposited activity due to Po^{212} to the total deposited activity observed between the energy span from 5.5 to 9.0 Mev.

Figure 17 is a plot of the data contained in Table 5 showing excellent agreement among the net cpm values and also showing the rate of increase of deposited background activity.

FIG. 17
CORRECTION FOR VARIABLE BACKGROUND ACTIVITY DEPOSITED IN COUNTER

Table 5

NET COUNTING RATE AFTER CORRECTING FOR DEPOSITED BACKGROUND

Time	Counts per Minute			
	Total between 5.5 and 9.0 Mev	Total Due to Po^{212}	Deposited Background	Net, Due to ($\text{Rn}^{220} + \text{Po}^{216}$)
12:00	3214	15	81	3133
12:40	3278	17	92	3186
1:15	3259	27	146	3113
2:09	3234	41	222	3012
3:30	3398	51	277	3121
4:30	3518	72	391	3127
5:00	3528	71	386	3142
6:18	3573	90	489	3084

The standard deviation in the net counting rate due to Rn^{220} and Po^{216} , based on the above data, is $\sigma = \pm 1.5\%$ or 3115 ± 47 cpm.

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