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NOVEL THERMAL METHODS FOR CHARACTERIZING CLAYS AND URANIUM ORES

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ABSTRACT

Simple, inexpensive, evolved gas procedures are described for simultaneously and selectively detecting the water, carbon dioxide, and/or ammonia given off by heated clay or ore samples Water vapor is detected by means of a commercially available relative humidity sensor. Carbon dioxide and ammonia are sensed by a new technique in which these effluent gases, entrained in a carrier gas stream, are interfaced with a liquid water phase. Dissolution of CO_2 or NH_3 in the water results in pH changes which are detected by a glass—reference electrode pair. The humidity sensor and pH cell are conveniently used in tandem with a thermal conductivity cell (for total evolved gas detection), with the evolved gas stream taken optionally from a DTA apparatus to allow simultaneous recording of thermal changes taking place in the heated sample

INTRODUCTION

Thermal methods have been much used in the study and characterization of naturally occurring clays. Surprisingly, however, there has been less use of such procedures in characterizing more complex materials which contain clay as a major fraction. Uranium ores found in the western United States contain typically ca. 10 wt.% clay and fall in this general category.

The thermal method which has been most used in the past for characterizing clays has been differential thermal analysis (DTA) [1]. Used alone, DTA curves can be difficult to interpret unambiguously, however, because of the nonspecific nature of the technique. DTA supplemented by effluent gas analysis (EGA) [2] results in some improvement since evolution of volatile thermal products can now be distinguished from other possible sources of thermal peaks. However, the usual gas thermal conductivity cell used in effluent gas work is, itself, nonspecific, making identification of individual gaseous products difficult without resort to ancillary information.

In the present work we sought to improve the usual DTA—EGA technique by incorporating additional EGA sensors which are specific, or at least selective, for individual volatile products formed on heating. Methods for achieving this objective are, of course, already known. One example is the use of a mass spectrometer [2] to continuously monitor effluent gas composition. In

TABLE 1

Volatile products from heated ores

	Source
H_2O	Clay water of hydration Clay dehydroxylation
CO_2	Metal carbonates ($CaCO_3$) associated with clay fraction
NH_3	Decomposition of ammonium ions introduced into clay fraction by ion exchange

the present work, however, emphasis was on the use of simpler and less expensive means which might ultimately be used in the field rather than in a well-equipped laboratory.

Table 1 lists the principal gaseous products which are evolved upon heating a uranium ore. Water is given off by the clay content of the ore in two distinct temperature regions. At the lower temperatures, water of hydration vaporizes; at higher temperatures hydroxyl groups present as part of the clay structure interact to evolve additional water. In addition to the clay content, ores from some locations also contain appreciable carbonate which gives rise to CO_2 on heating (Table 1).

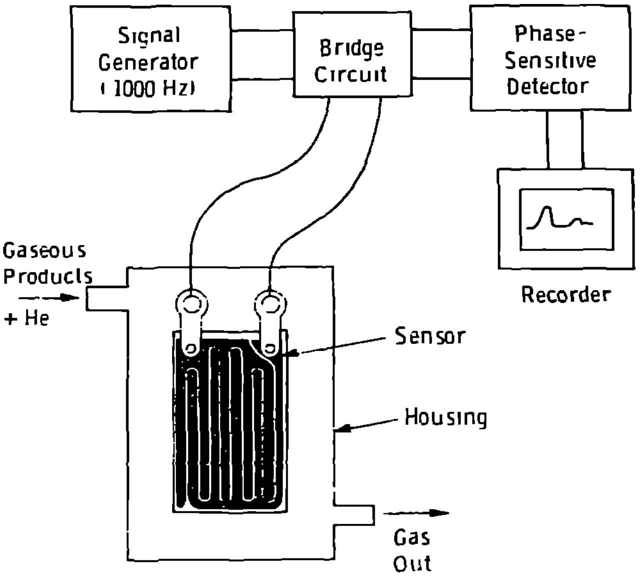
The third substance listed in Table 1, viz., NH_3, results from ammonium ions introduced into the clay fraction during extraction of the uranium content of the ore. One method for isolating uranium from ore involves treatment with carbonate-containing solutions in the presence of an oxidant to form one or more soluble uranium carbonate species [3]. The formation of one such complex is shown in reaction (1).

$$UO_2^{2+} + 3\ CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} \qquad (1)$$

The preferred source of the carbonate ion reactant is a water solution of ammonium bicarbonate (which contains an equilibrium concentration of carbonate ion). The presence of ammonium ion allows, as a side reaction, ion exchange with cations such as sodium which are native to the clay, resulting in a partially ammoniated insoluble clay fraction.

RESULTS AND DISCUSSION

In the following we will describe the means we have chosen to detect and to distinguish among the three volatile reaction products listed in Table 1, and will give examples of the use of these procedures. For the detection of water we have employed a commercially-available relative humidity (RH) sensor. The specific detector employed is sold by the Phys-Chemical Research Corporation. It consists of a polystyrene wafer which has been treated by the manufacturer to introduce hydrophilic groups on the surface.



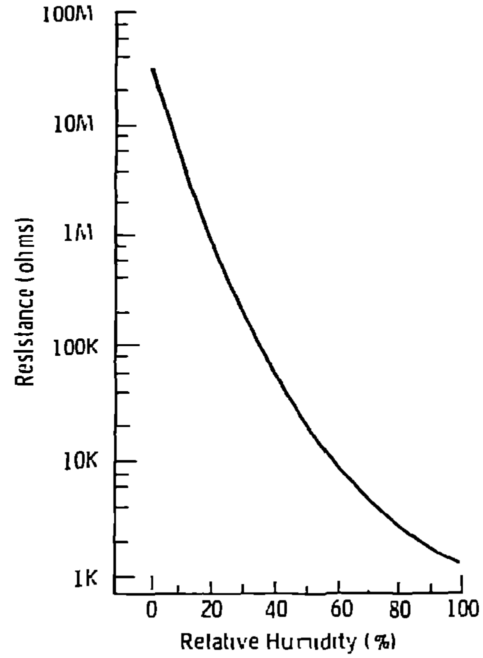


Fig. 1 Humidity sensing portion of the effluent gas apparatus.

Fig 2. Resistance vs. relative humidity curve for the humidity sensor used in the present work (Replotted from data supplied by the manufacturer.)

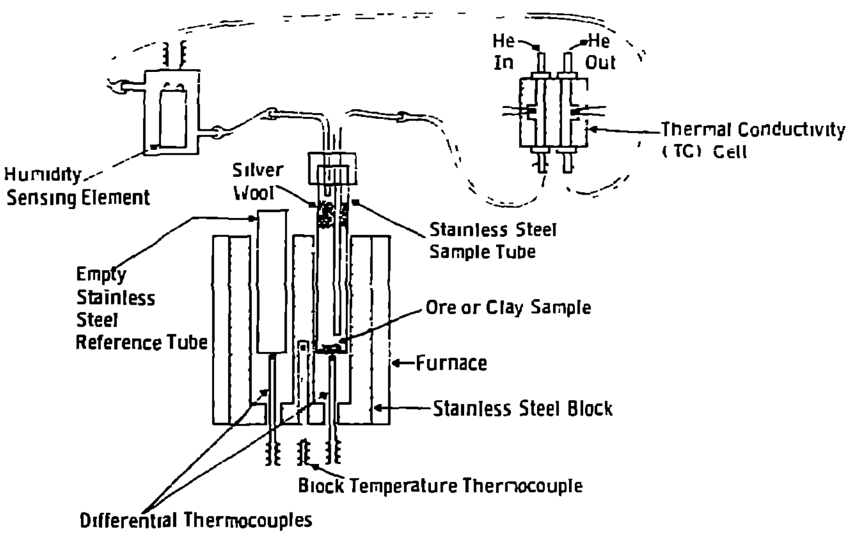


Fig. 3. Experimental arrangement for simultaneous differential thermal analysis and effluent gas analysis

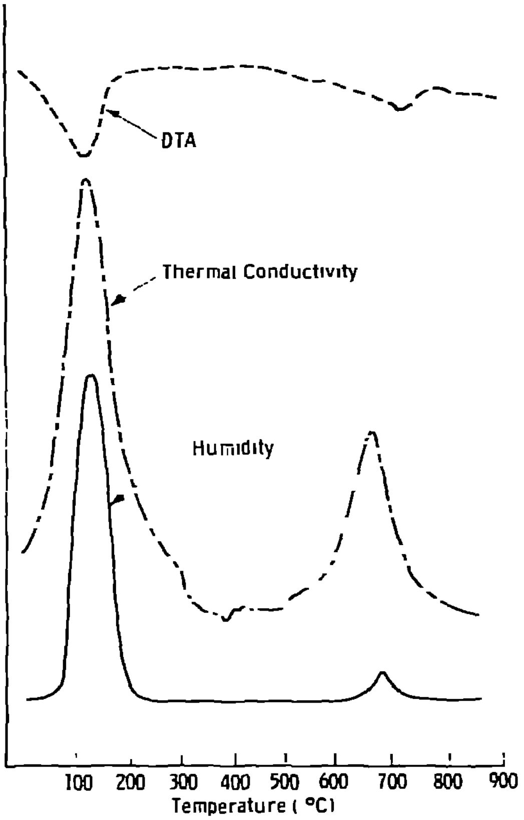


Fig. 4. Thermal analysis curves for 200 mg API clay mineral standard No 27.

The element responds to changes in relative humidity by corresponding changes in electrical impedance when incorporated into an AC bridge circuit, as shown in Fig. 1. Electrical response is not linear with respect to relative humidity but is rather logarithmic, as shown in Fig. 2 for a previously unused sensor. Calibration of the RH element changes slowly with use but an individual sensor remains sufficiently sensitive for qualitative identification of water vapor over a period of months.

Figure 3 gives schematically the experimental arrangement for simultaneously obtaining DTA, relative humidity, and gas thermal conductivity curves. The ore or clay sample is heated in a stainless steel tube with linear programming of temperature (10°C min^{-1}). Evolved gases are flushed from the heated cell with pure helium and then passed through the RH and TC cells, used in tandem. The DTA portion of the apparatus has been previously described in details [4,5].

In Fig. 4 we show DTA, RH, and TC curves obtained simultaneously by means of the apparatus of Fig. 3. The curves here refer to a standard clay mineral sample previously characterized by Kerr et al. [6]. The RH curve establishes unambiguously that the major peaks observed in the DTA and TC curves are all due to the evolution of water.

For the selective detection of evolved carbon dioxide or ammonia from uranium ores, we have devised a different procedure which can be made specific for either acidic or basic products entrained in a carrier gas stream. The method is based on contacting the thermally evolved gas with a flowing stream of liquid water in a cell which contains a glass—reference electrode pair for pH measurement.

Figure 5 diagrams the experimental arrangement employed. Water, with a small amount (1% wt./vol.) of sodium chloride added to increase electrical conductivity and previously adjusted to pH = 7.0 ± 0.1 with dilute HCl or NaOH, is pumped through the glass measuring cell at about 20 ml $\min^{-1}$. The effluent gas stream from the DTA apparatus is simultaneously bubbled through the cell at 100 ml $\min^{-1}$. Water and undissolved gas exit together to a collection bottle.

Figure 6 shows, in idealized form, the type of plots expected from the apparatus of Fig. 5. When measured pH is plotted (automatically with a recording pH meter) vs. DTA furnace temperature, an evolved acidic gas, such as CO_2, entrained in the flowing carrier gas will cause a peak directed toward lower pH values from the base line at pH = 7. A basic gas, such as ammonia, will produce a peak in the opposite sense. The reason for employing a flowing, as opposed to a static, volume of water as the absorbent is to ensure that observed pH values will return promptly to the base line as soon

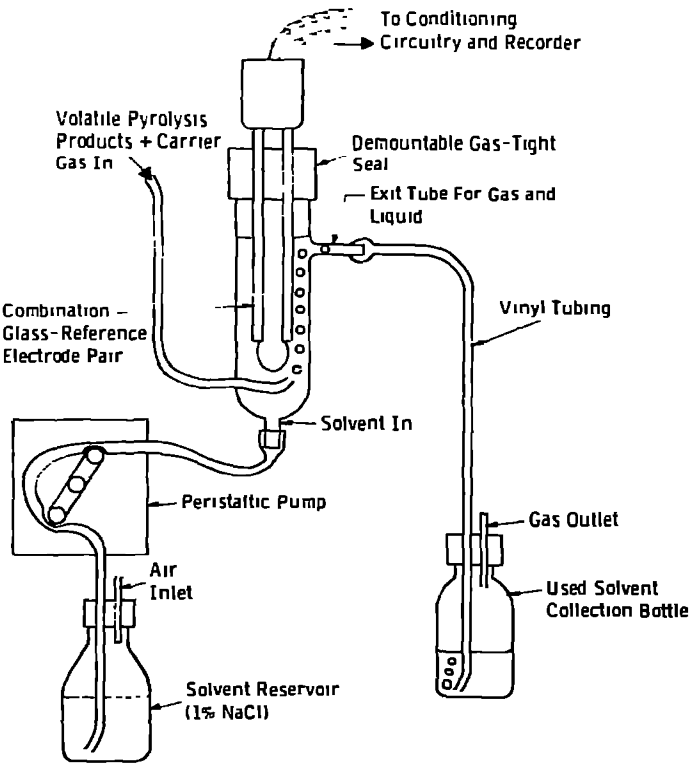


Fig. 5. Detail of apparatus used to obtain pH—EGA curves.

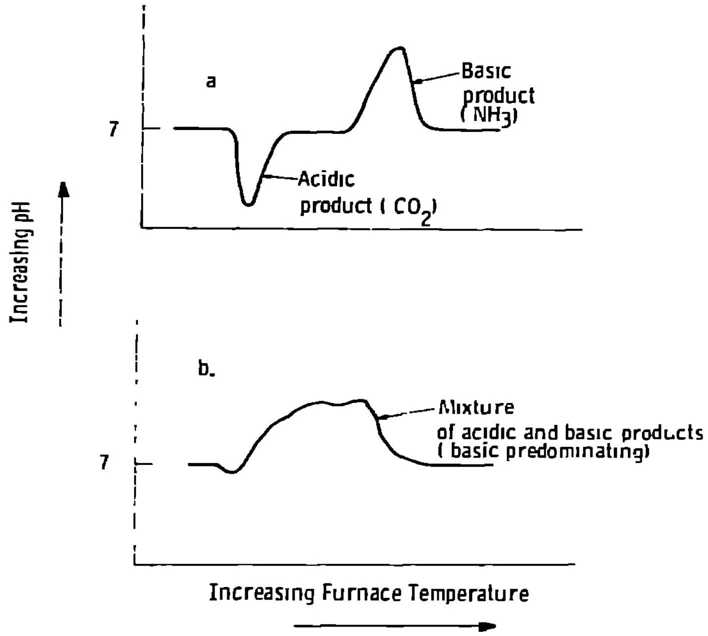


Fig. 6. Idealized EGA—pH curves for a system utilizing a flowing aqueous absorbent. (a) Acidic and basic products produced in non-overlapping temperature regions. (b) Acidic and basic products in overlapping temperature regions with base predominating over most of the temperature range.

as evolution of the respective gases is complete *.

Provided the temperature regions for successive gas evolution are sufficiently widely spaced, our pH technique is capable of detecting both acidic and basic gaseous products in a single run, to give a record such as that shown in Fig. 6a. Difficulties of interpretation arise, however, when acids and bases are evolved simultaneously or in overlapping temperature regions. A plot which might be obtained under these conditions is shown schematically in Fig. 6b.

We have been able to circumvent this difficulty through the use of selective solid absorbents used upstream of the pH cell to remove either the basic or acidic components of the mixture. The two adsorbents we have found most useful are sodium hydroxide pellets, to remove CO_2 and other acidic gases, and anhydrous $CaSO_4$ (Drierite) to remove ammonia. Both NaOH and $CaSO_4$ also remove any water vapor which may be present in the carrier gas. The adsorbents are therefore used downstream from the humidity detector when this is employed simultaneously with the pH cell. The overall system

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* Early EGA—pH work in this laboratory employed static absorption solutions (see ref. 7). Curves obtained in this manner are more difficult to interpret than are those which result from the preferred technique described here.

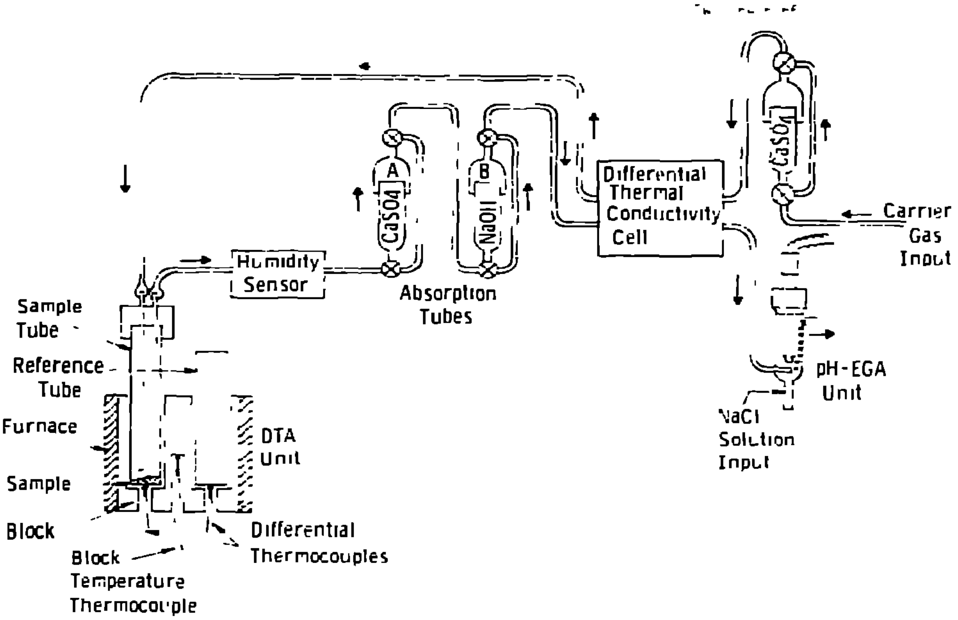

Fig. 7. Thermal analysis apparatus for simultaneously recording DTA, water evolution, gas thermal conductivity, and pH—EGA curves Bypassable adsorption tubes allow the selective removal of water and/or volatile acidic or basic pyrolysis products from the carrier gas stream. Short arrows show the path for gas flow.

which employs water sensor, pH cell, and thermal conductivity cell (for nonspecific detection of total evolved gas) is diagrammed in Fig. 7.

The response of the pH cell to absorbed gas is not linear with dissolved gas concentration for either CO_2 or NH_3. Rather, the total dissolved gas concentration ($[CO_2]_T$ or $[NH_3]_T$) is related to observed pH by eqns. (2 and 3) below.

$$[CO_2]_T = \frac{[H^+]^2 - K_W}{K_C} + [H^+] - K_W/[H^+] \tag{2}$$

$$[NH_3]_T = \frac{K_W^2/[H^+]^2 - K_W}{K_H} - [H^+] - K_W/[H^+] \tag{3}$$

where K_W is the water constant, K_C is the acid ionization constant of dissolved carbon dioxide, and K_H is the hydrolysis constant characteristic of ammonia. (See the Experimental section for derivation of these equations.) The righ-hand side of both equations reduces to zero for pH = 7. The above equations are used to calculate the curves in Fig. 8, where $p[CO_2]_T$, $p[NH_3]_T$, and pH represent the negative logarithms of $[CO_2]_T$, $[NH_3]_T$, and $[H^+]$, respectively.

Figure 9 shows the results obtained by our water-absorption pH technique

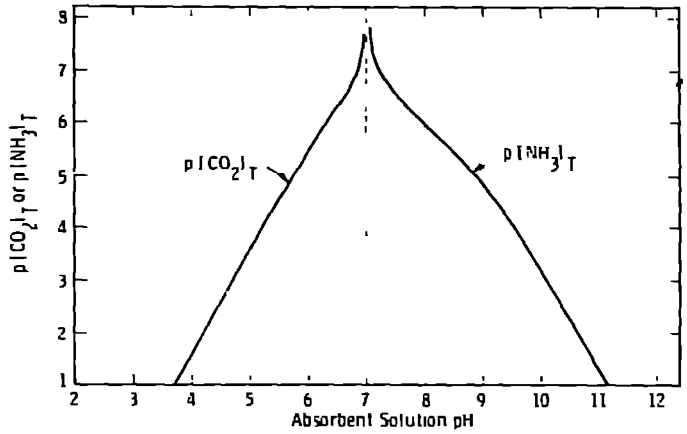

Fig. 8. The quantities $p[CO_2]_T$ and $p[NH_3]_T$ as functions of solution pH

for the thermal decomposition of a variety of pure metal carbonates. The indicated temperature regions for evolution of carbon dioxide are in reasonable agreement with results obtained by other thermal techniques [8].

In interpreting EGA—pH curves such as those shown in Fig. 9, it is necessary to keep in mind the logarithmic nature of the ordinate. Figure 10 compares the EGA—pH curves for zinc and cupric carbonates with corresponding derived curves which are linear in dissolved CO_2 concentration (calculated by means of eqn. (2)). The derived curves of Fig. 10 show the bulk of the evolved CO_2 to be given off over narrower temperature regions than might be inferred by a casual inspection of Fig. 9.

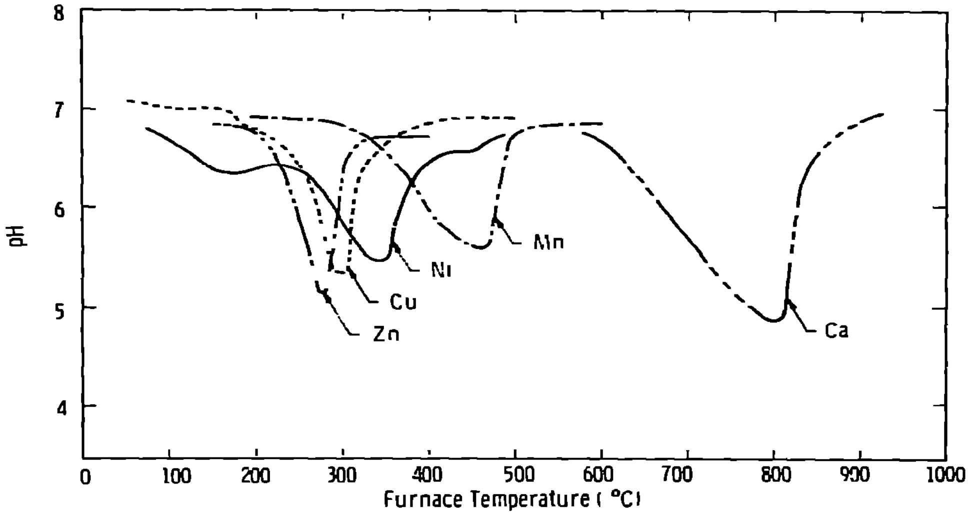

Fig. 9. EGA—pH curves for 200 mg samples of divalent metal carbonates heated in flowing helium.

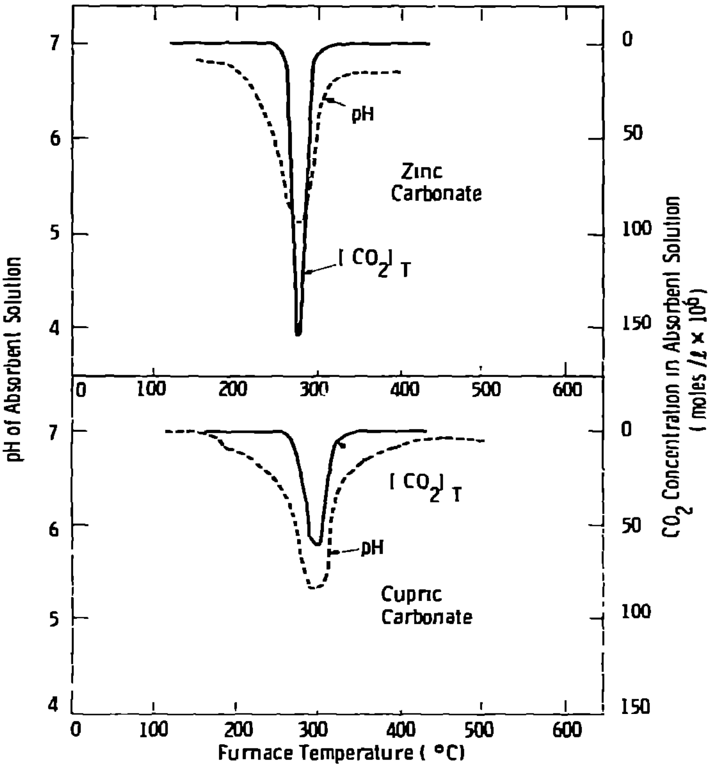

Fig 10. Alternate means for presenting the effluent gas results

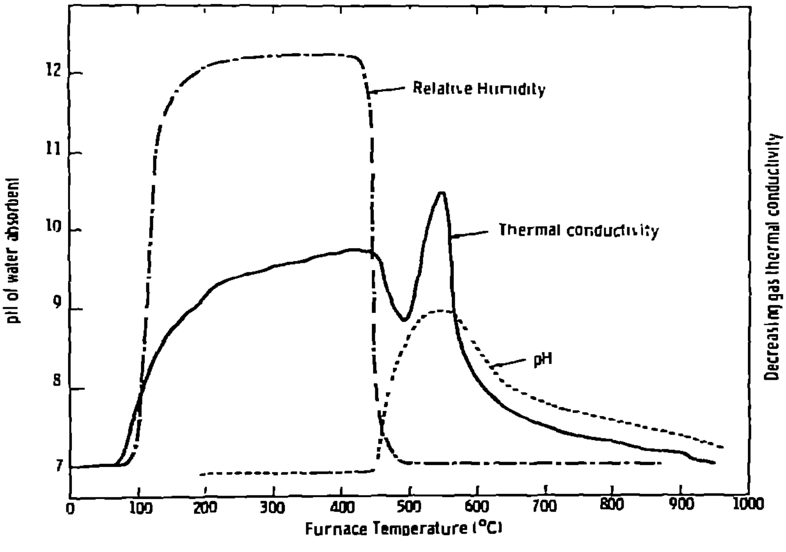

Fig. 11. Effluent gas curves for 200 mg aluminum sulfate heated in flowing helium. The curves were obtained simultaneously for a single sample.

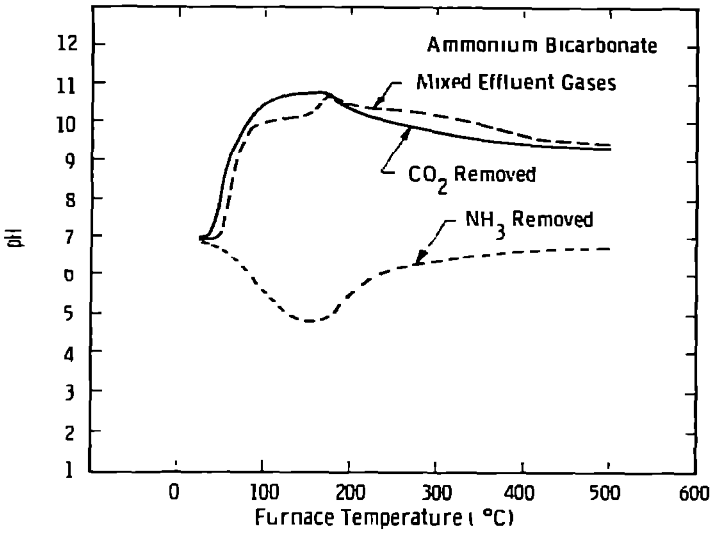

Fig 12 EGA—pH curves for three successive 200 mg samples of NH_4HCO_3 heated in flowing helium. For two of the runs, acidic or basic components of the effluent gas mixture were removed by solid NaOH or anhydrous $CaSO_4$, respectively, prior to measurement.

Figure 11 gives simultaneously recorded EGA curves for a heated sample of hydrated aluminum ammonium sulfate. The thermal conductivity curve shows that volatile products are given off in two distinct temperature regions but does not distinguish between water vapor and ammonia evolution. The relative humidity and pH curves, however, indicate clearly the evolution of water in the lower temperature region followed by ammonia at higher temperatures.

In Fig. 12 we demonstrate the use of solid adsorbents in those instances where acidic and basic pyrolysis products are given off in the same temperature region. Ammonium bicarbonate decomposes with the simultaneous formation of NH_3 and CO_2. As shown in Fig. 12, only the NH_3 content of the mixture is detected when solid adsorbent is not employed upstream of the pH detection cell. The presence of CO_2 is completely masked. When the adsorbents $CaSO_4$ and NaOH are used separately in consecutive runs, however, CO_2 and NH_3 are detected separately as indicated in the figure.

The final three figures demonstrate the use of the EGA—pH technique with uranium ores heated in flowing helium. In Fig. 13 we show results obtained for an ore known from other evidence to contain appreciable calcium carbonate. The EGA—pH curve surprisingly shows two well-resolved peaks for the evolution of CO_2. The higher temperature of these peaks appears to be due to the decomposition of $CaCO_3$. (Note comparison with the EGA—pH curve for pure $CaCO_3$, also given in Fig. 13.) The second and lower temperature peak characteristic of the ore must be ascribed to an additional metal carbonate phase, of as yet unknown composition, the presence of which had not previously been suspected.

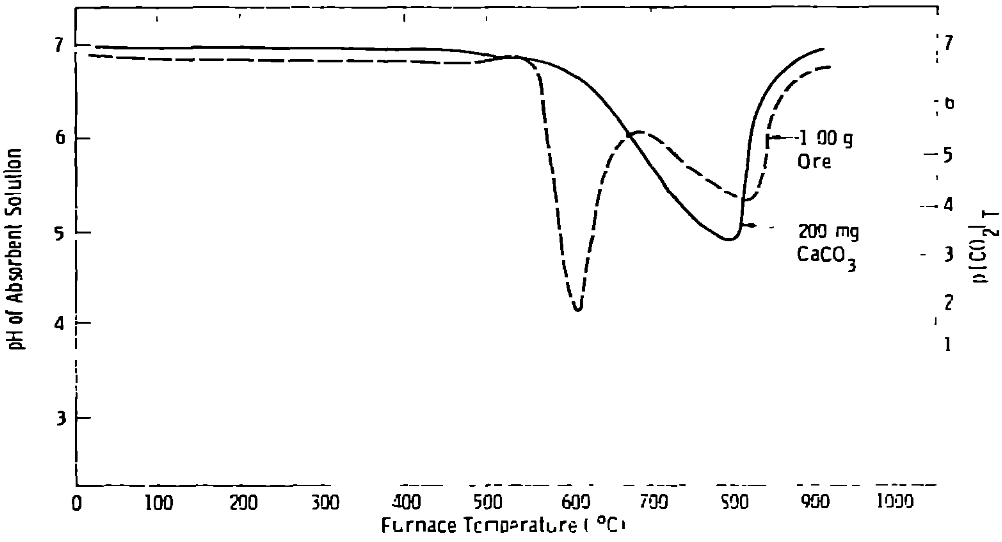

Fig 13. A comparison of EGA—pH results for pure $CaCO_3$ with those for an unleached uranium ore known to contain carbonate.

Figure 14 again shows the EGA—pH curve characteristic of the same ore but this time compares it with that of a second specimen of an identical ore which has been exposed to ammonium bicarbonate solution. The new EGA—pH peak, in the 400—600°C region, clearly represents the decomposition of ammonium groups introduced into the clay fraction of the ore by ion exchange during the leaching process.

In Fig. 15 we show EGA—pH curves obtained for ore samples from a separate location and which differ also from the ore of Figs. 13 and 14 in not having a detectable carbonate content. The specimens of Fig. 15 differ between themselves only in the extent to which cations native to the ore clay content have been replaced by ammonium ion *. The EGA—pH curves of Fig. 15 show our thermal procedure to be capable of detecting widely differing ammonium contents, with a lower limit in the p.p.m. range. Sensitivity to low NH_4^+ concentrations could probably be increased by at least an additional factor of 10 by using a larger ore sample.

In summary, we have shown that it is possible to distinguish the three major volatile pyrolysis products from uranium ores (H_2O, CO_2, and NH_3) with equipment simple and inexpensive enough to be considered for use in the field. The same procedures should also prove useful in the thermal study of numerous other materials which evolve water, CO_2, and/or NH_3 upon heating. Although we have stressed the qualitative identification aspects of the technique, it also seems possible that the EGA—pH method could be

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* The indicated NH_4^+ contents were obtained by conventional wet chemical means

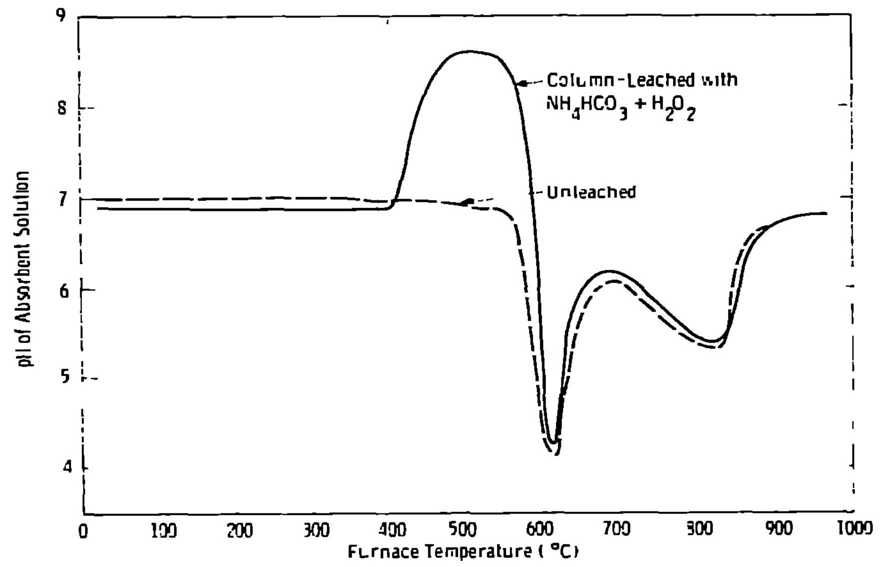

Fig. 14. A comparison of EGA—pH curves for 1 g samples of uranium ore heated in flowing helium.

employed quantitatively for the determination of CO_2 and/or NH_3. This could be most easily done by electronic processing of the pH electrical signal, on a real time basis, in order to record directly, dissolved CO_2 or NH_3 concentrations (rather than pH) vs. furnace temperature (see Fig. 10).

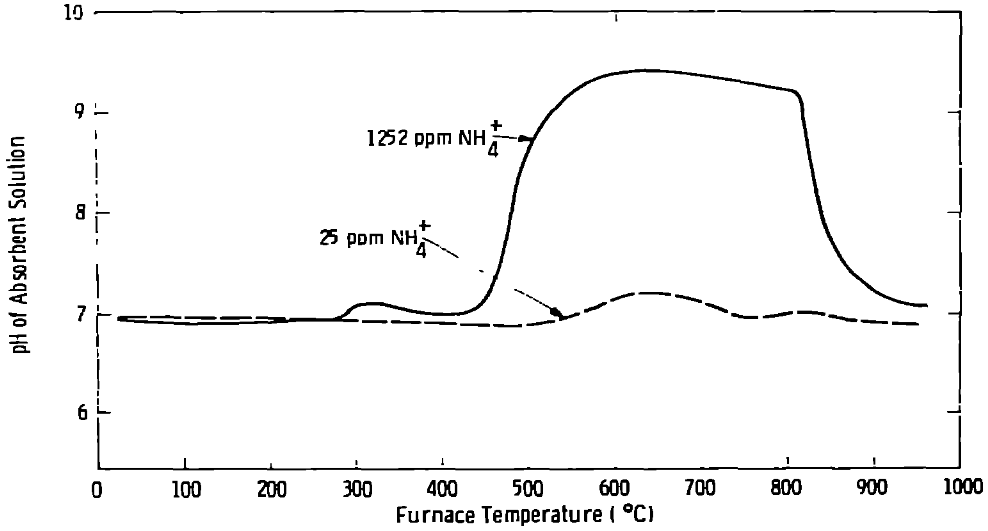

Fig. 15. EGA—pH curves for 1.00 g samples of uranium ore containing the concentrations of bonded ammonium ion indicated. The specimens are from the same ore deposit but have been exposed to differing quantities of ammonium bicarbonate solution.

EXPERIMENTAL

Apparatus

The unheated portions of the apparatus shown in Figs. 3, 5, and 7 were joined by 1/8-in. vinyl tubing equipped with Luer joints (Ace Glass, Vineland, N.J.). The entrant and exit tubes for the sample tube (Fig. 3) were stainless steel. A wad of silver wool was used in the upper part of the sample tube to absorb any sulfur-containing gases which might be given off. These impurities are stated by the manufacturer (Phys-Chemical Research Corp., New York) to be deleterious to the operation of the humidity sensor (Model PCRC-11).

A special 1000 Hz power supply and phase-sensitive detector was constructed in this laboratory for use with the humidity sensing element. Experience with the element, however, has convinced us that the very much simpler circuitry suggested by the sensor manufacturer would be adequate for the present applications.

A Sensorex (Irvine, Ca.) Model P/N S200C combination glass—reference electrode is used in the glass cell of Fig. 5, in conjunction with a Cole—Parmer (Chicago) Model 7016 peristaltic pump head and 20 r.p.m. motor. The EGA—pH cell of Fig. 5 contains about 2 ml of liquid at any given time, with the electrode in place and helium * flowing. A Gow—Mac (Madison, N.J.) Model 10-677 thermistor type gas thermal conductivity cell was used in the setup of Fig. 7.

Materials

The divalent metal carbonates MCO_3 (Fig. 9) were the purest available. They were purchased from Fisher Scientific Co. (Pittsburgh, Pa.) or Matheson, Coleman and Bell (Norwood, Ohio). The cupric compound is stated by the supplier (Matheson) to be a basic salt of composition $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$.

The reference clay mineral standard used in the present work was montmorillonite No. 27 as characterized by the American Petroleum Institute Clay Minerals Standards Project No. 49. It was purchased from Wards Natural Science Establishment, Rochester, N.Y. and subsequently ground to pass a 100 mesh sieve. Uranium ore samples were kindly supplied by the Wyoming Minerals Corp. (Denver, Co.). They were also ground to pass a 100 mesh screen.

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* The operations of the EGA—pH and humidity sensing portions of our apparatus are not affected by the substition of other inert gases for helium in the carrier stream. When the use of a thermal conductivity cell in tandem is desired, however, helium is required for maximum TC sensitivity.

Relationships between dissolved gas concentration and measured pH (Fig 8)

Solutions at pH values <7 contain dissolved molecular CO_2 and HCO_3^- ion (CO_3^{2-} exists at negligible concentrations in this pH region. The concentration of H_2CO_3 is also negligible [3,9]. The total concentration of carbonate species, $[CO_2]_T$, can therefore be taken as (4), below. Other pertinent relationships are listed as (5—7)

$$[CO_2]_T = [CO_2] + [HCO_3^-] \tag{4}$$

$$[H^+] = [HCO_3^-] + [OH^-] \tag{5}$$

$$K_W = [H^+][OH^-] = 1 \times 10^{-14} \tag{6}$$

$$K_C = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.4 \times 10^{-7} \tag{7}$$

Equation (5) expresses the charge balance necessary for electrical neutrality of the solution, while eqns. (6 and 7) refer to the ionization behavior of water and CO_2, respectively. The numerical value of K_C is that listed by Butler [9].

From eqns. (5 and 6) it follows that

$$[HCO_3^-] = [H^+] - K_W/[H^+] \tag{8}$$

Substitution of eqn (8) for $[HCO_3^-]$ in eqn. (7) and rearrangement gives eqn. (9)

$$[CO_2] = \frac{[H^+]^2 - K_W}{K_C} \tag{9}$$

Finally, substitution of eqns. (8 and 9) for $[HCO_3^-]$ and $[CO_2]$, respectively, into eqn. (4) gives the desired relation (2).

The derivation of the corresponding expression for dissolved ammonia is similar to that just given. Pertinent equations are (6), above, and (10—12), below

$$[NH_3]_T = [NH_3] + [NH_4^+] \tag{10}$$

$$[NH_4^+] + [H^+] = [OH^-] \tag{11}$$

$$K_H = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.78 \times 10^{-5} \tag{12}$$

Equation (11) expresses charge balance, while eqn. (12) refers to the hydrolysis equilibrium (13)

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{13}$$

Substitution of $K_W/[H^+]$, from eqn. (6), for $[OH^-]$ in eqn. (11) and rearrangement gives eqn. (14)

$$[NH_4^+] = K_W/[H^+] - [H^+] \tag{14}$$

Rearrangement of eqn. (12), followed by substitution of the expressions (6) and (14) for $[OH^-]$ and $[NH_4^+]$, respectively, gives eqn. (15)

$$[NH_3] = \frac{K_W^2/[H^+]^2 - K_W}{K_H} \tag{15}$$

Substitution of eqns. (14 and 15) into eqn. (10) gives the desired expression (3), above, relating the total dissolved ammonia concentration to hydrogen ion concentration.

Equation (3) is applicable only for pH > 7 and only for those instances where the single basic gaseous product is ammonia. The latter is a reasonable assumption for all the work reported here.

ACKNOWLEDGEMENTS

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REFERENCES

1 R.C. Mackenzie (Ed), The Differential Thermal Investigation of Clays, Mineralogical Society, London, 1957.
2 W. Lodding (Ed), Gas Effluent Analysis, Marcel Dekker, New York, 1967.
3 A.J Panson and R.G Charles, in Proceedings of the American Nuclear Society Topical Meeting on Energy and Mineral Resource Recovery, CONF-770440, U S. Department of Energy, Washington, D.C., 1977, p. 728
4 R.G Charles, Trans. Am. Nucl. Soc., 19 (1974) 107
5 R.E. Witkowski and R.G. Charles, in Proceedings of the International Conference on Liquid Metal Technology in Energy Production, CONF 760503-P2, U S Department of Commerce, Springfield, Va., 1976, p 860.
6 P F. Kerr, J.L. Kulp and P K. Hamilton, Differential Thermal Analysis of Reference Clay Mineral Specimens, Preliminary Report No. 3, American Petroleum Institute Project 49, 1949.
7 R.G. Charles, J. Inorg. Nucl. Chem., 28 (1966) 407.
8 R.L. Webb and J.E. Kruger, In R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol 1, Academic Press, New York, 1970, p. 303.
9 J.M Butler, Ionic Equilibrium, Addison-Wesley, Reading, Mass , 1964.