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ENGINEERING DEVELOPMENT OF FLUID-BED
FLUORIDE VOLATILITY PROCESSES

Part 11. Off-gas Analysis

by

**D. Ramaswami, L. J. Anastasia,
N. M. Levitz, W. J. Mecham,
and A. A. Jonke**

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Chemical Separations
Processes for Plutonium
and Uranium

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

July 1968

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SUMMARY

Fluid-bed fluoride-volatility processes are being developed for the recovery of fissionable values from spent nuclear-reactor fuels of low- and high-enrichment types. In these processes, the fissionable values are converted to volatile fluorides for separation and purification. The off-gas streams from the various process reaction vessels may contain one or more of the following gases: uranium hexafluoride, plutonium hexafluoride, bromine pentafluoride, hydrogen fluoride, hydrogen chloride, fluorine, bromine, hydrogen, oxygen, and nitrogen. Many of these gases are reagents or products of the chemical reactions, and analyses of the reactor off-gases for these constituents are necessary to provide information on the rates of reaction, the extent of reaction, and the utilization of reagents.

Thermal-conductivity methods have been developed and applied at Argonne National Laboratory for the continuous analysis of reactor off-gases and for possible application to automatic process control of the reactor. This report summarizes the application, operation, and performance of commercially available thermal-conductivity cells as used in six bench-scale and engineering-scale installations. Nickel cells with nickel wire filaments withstood the corrosive environments sufficiently so that stable operating characteristics and therefore a satisfactory operating lifetime can be anticipated for these cells in a fluoride-volatility process.

I. INTRODUCTION

Fluid-bed fluoride-volatility processes for the recovery of uranium and plutonium from spent nuclear-reactor fuels are being developed at Argonne National Laboratory. These processes are based on the conversion of uranium and plutonium to volatile hexafluorides, which can be separated from cladding and fission products for purification. These processes are considered applicable to a wide variety of fuels and are being developed for two types of fuel which are of interest. One fuel is

low-enrichment uranium dioxide-plutonium dioxide clad in either Zircaloy or stainless steel. The other is highly enriched uranium, alloyed with Zircaloy or aluminum.

The initial steps in the process are similar for both types of fuel.¹ In the initial decladding or separation step, the cladding or alloying material is separated from the fuel material. In the second processing step, uranium and plutonium (in the case of low-enrichment fuel) and uranium (in the case of high-enrichment fuel) are fluorinated to the volatile hexafluorides. In both process steps, highly exothermic gas-solid reactions are carried out with multicomponent gas streams in fluid-bed reactors. The chemical-reaction rates depend highly on the conditions prevailing in the fluid-bed reactors. Proper control and monitoring of the progress of reaction require continuous in-line gas analysis. The method of analysis chosen must be reliable and compatible with the process atmospheres and must also be suitable for remote operation when irradiated fuels are processed. During continued use, the detector should have adequate response; adequate corrosion resistance, and stable operating characteristics.

Differences in density, viscosity, magnetic susceptibility, and thermal conductivity between gaseous mixtures are some of the specific properties that have been used in recently developed methods of analysis. One of the most easily measured properties is the thermal conductivity of gases. The analysis of gas with temperature-regulated thermal-conductivity cells is simple, reliable, and relatively fast.

This report summarizes (1) current practice in measuring thermal conductivity of gases and (2) the application of thermal-conductivity methods to the analysis of off-gases from fluid-bed reactors and to the control of fluid-bed fluorinators used in the development of fluoride-volatility processes at Argonne National Laboratory.

II. THEORY

The physical property of thermal conductivity is inherent in all matter. Materials of low thermal conductivity are used as insulators to prevent either the emission or absorption of heat energy from a region of desired temperature stability. Materials of high thermal conductivity are used to enhance transfer of heat energy from regions of high heat generation or absorption. Thus, the quantitative determination of this property is of great importance in practical applications. The reproducibility of this property also makes it useful as an indicator of the quality of a certain material. This aspect is exploited in the analysis of gas composition.

The analysis of gaseous mixtures by thermal-conductivity methods depends on the ability of gas molecules to transfer heat by diffusion and

collision. This ability is different for every gas or gas mixture; hence, the method is nonspecific and ideally suited for binary gas mixtures. The method is also applicable to the analysis of a single gas in multicomponent mixtures, provided that the mole ratios of other species in the mixture remain relatively constant.

A. Definition of Thermal Conductivity

The formal definition of thermal conductivity of a gas equates it to a quantity of heat transferred in unit time between two unit surfaces in a gas when they are unit distance apart and have a temperature difference of 1° between them. That is,

$$k = -q_x \frac{dx}{dt}, \quad (1)$$

where

k is thermal conductivity,

q_x is heat flux,

t is temperature,

and

x is distance in the direction of heat flow.

The energy-transport coefficient, k , is analogous to the momentum-transport coefficient, viscosity (μ). These coefficients are related² for polyatomic gases by Eucken's semiempirical equation,

$$k = \frac{\mu}{M} (C_p + 1.25R), \quad (2)$$

where

M is molecular weight,

C_p is molal specific heat at constant pressure,

and

R is the universal gas constant.

Viscosity of polyatomic gases may be estimated by the equation³

$$\mu = \frac{2.6693 \times 10^{-5} \sqrt{MT}}{\sigma^2 \Omega \mu}, \quad (3)$$

where

μ is viscosity, poises;

T is absolute temperature, °K;

σ is collision diameter, Å;

and

Ω is collision integral.

By substitution of Eq. 3 into Eq. 2, the following relation between thermal conductivity and molecular weight is obtained:

$$k = 2.6693 \times 10^{-5} \frac{\sqrt{T}}{\Omega \mu} \frac{1}{\sqrt{M}} \frac{1}{\sigma^2} (C_p + 1.25R). \quad (4)$$

Equation 4 is useful as a generalized equation for the estimation of thermal conductivity of polyatomic gases in the absence of experimental data.

B. Thermal-conductivity Cells

To detect a change in thermal conductivity due to a change in the composition of a gas, heated filaments or thermistors are exposed to the gas mixture in the thermal-conductivity cell. The filaments or thermistors are used as the four resistors in a resistance-sensitive Wheatstone Bridge. When this circuit is exposed to a resistance change in any of its four arms, a small potential difference can be detected across the previously balanced bridge. Heat input and heat losses from the cell are fixed so that resistance changes are proportional to changes in the gas thermal conductivity.

1. Wheatstone Bridge Circuit

In the usual application of thermal-conductivity cells to the analysis of a gas, the four heated filaments used as the legs of the Wheatstone Bridge are housed in a metal block. The cell filaments are normally constructed from metals with a high-temperature coefficient of resistivity. The reference gas of known composition is passed over two filaments of the bridge (reference side of cell), and the sample gas of unknown composition is passed over the other elements (sample side). Displacement from thermal equilibrium between the reference and the sample sides of the cell unbalances the bridge. The degree of imbalance, measured by a potentiometer, is a function of the thermal conductivity and the concentration of the component of interest in the sample gas.

Fig. 1. Cell Filaments Connected to Form a Wheatstone Bridge Circuit

In operation, a low dc voltage is applied across the Wheatstone Bridge circuit, as shown in Fig. 1. The applied voltage maintains the filaments at a relatively high temperature, and an indicator and/or recorder are used to measure the output voltage of the cell. At any time,

$$I_1(R_{R1} + R_{S1}) = I_2(R_{R2} + R_{S2}). \quad (5)$$

If the bridge is electrically balanced,

$$I_1 R_{R1} = I_2 R_{S2}$$

and

$$I_1 R_{S1} = I_2 R_{R2},$$

or, if the currents are eliminated, $R_{R1}R_{R2} = R_{S2}R_{S1}$. This equation shows that the imbalance caused by displacement from thermal equilibrium with four filaments in the bridge depends on the product of resistances in the sample and reference sides of the cell; therefore, the cell is quite sensitive to differences in thermal conductivities of the reference and sample gases and permits the measurement of very small concentration changes.

2. Sensitivity

In a single filament,

Power dissipated = $I^2 R$ (by Joule's Law).

The voltage drop across each filament is $E/2$, and since

$$I = E/R,$$

$$\text{power dissipated} = \frac{E^2}{4R}, \quad (6)$$

where

I is the current through each filament,

E is the applied voltage,

and

R is the resistance of each filament.

This dissipated power may be equated^{4,5} as follows:

$$\frac{E^2}{4R} = (2\pi kL + fC_p) a \Delta T, \quad (7)$$

where

L is filament length,

ΔT is the difference between temperature of wire and block,

f is flowrate,

and

a is a geometrical constant given by $a^{-1} = \ln(r_c/r_w)$,

where

r_c and r_w are the radii of the channel and wire, respectively.

Equation 7 exhibits the desired linear dependence upon the thermal conductivity of the gas.

Now, if a fraction of the carrier gas, dX , is displaced by an impurity gas, then the thermal conductivity and specific heat will be changed by an amount given approximately by

$$dk = (k_{\text{carrier}} - k_{\text{impurity}}) dX = \Delta k dX$$

and

$$dC_p = [C_{p(\text{carrier})} - C_{p(\text{impurity})}] dX = \Delta C_p dX.$$

Keeping power dissipation constant and differentiating Eq. 7 gives

$$0 = (2\pi kL + fC_p) a d\Delta T + (2\pi Ldk + f dC_p) a \Delta T.$$

If the change in ΔT is assumed to be solely due to a change in the temperature of the filament, dT_w , then

$$d\Delta T = dT_w.$$

Then, by substitution for dk , dC_p , and $d\Delta T$,

$$d\Delta T = dT_w = \frac{2\pi L\Delta k + f\Delta C_p}{2\pi Lk + fC_p} \Delta T dX.$$

The change of resistance in the wire is given by

$$dR = \alpha R dT_w,$$

where α is the thermal coefficient of resistance. The change in emf across the bridge⁵ is

$$dE = -(1/4)E \frac{dR}{R} = -(1/4)E\alpha dT_w.$$

If the sensitivity of the thermal-conductivity cell is defined as the fraction change in E per change in composition, $(dE/E)/dX$, then by combining the above equations, the following is shown:⁵

$$\frac{dE}{E} = -(1/4)\alpha dT_w = (1/4)\alpha \frac{2\pi L\Delta k + f\Delta C_p}{2\pi Lk + fC_p} \Delta T dX.$$

Also,

$$\Delta T = \frac{E^2}{4aR(2\pi Lk + fC_p)},$$

and

$$\frac{dE/E}{dX} = \frac{2\pi L\Delta k + f\Delta C_p}{a(2\pi Lk + fC_p)^2} \cdot \frac{\alpha E^2}{16R}.$$

The sensitivity then depends directly on the square of the applied voltage and inversely on the filament resistance and therefore increases directly as the dissipated power.

Since the sensitivity depends on E^2 , it is very critical that the applied voltage be held constant. Constant voltage is easily obtained with a stable power supply.

Thermal-conductivity cells are particularly sensitive to gas flowrates. This sensitivity⁵ can be given by

$$\text{Sensitivity to flowrate fluctuation} = \frac{C_p}{a(2\pi Lk + fC_p)^2} \cdot \frac{\alpha E^2}{16R}. \quad (8)$$

The stability⁵ of the thermal-conductivity cell is then defined as the sensitivity $(dE/E)/dX$ over the sensitivity to flowrate fluctuations and is given as

$$\text{Stability factor} = \frac{2\pi L\Delta k + fC_p}{C_p}. \quad (9)$$

Equation 9 indicates that a larger Δk (as defined previously) will provide greater stability. Therefore, a carrier gas and an impurity gas of widely differing thermal conductivities are desirable. This can be promoted by using a carrier gas such as hydrogen or helium whose thermal conductivity is very high in comparison to almost all other gases or gas mixtures.

Fig. 2

Types of Flow
Channeling for
Thermal-
conductivity Cells

The heated filaments of the thermal-conductivity cell can be placed in several positions with respect to the gas flow pattern, as shown in Fig. 2. Type A offers the advantage of rapid response to composition changes, but is quite sensitive to changes in flowrate. Type B depends on diffusion for its reading, thus giving a slower response than Type A but freedom from flowrate dependence. Type C is an attempt to compromise these advantages and drawbacks;

it is designed to achieve a fairly constant flow over the filament regardless of line flow and to maintain rapid replacement of gas past the resistor to facilitate rapid response. Type B thermal-conductivity cells have been used in the volatility-process studies.

To obtain maximum sensitivity and reliability in output data from the thermal-conductivity cell, the filaments are mounted in a metal block. The block keeps the sample and reference sides of the cell at the same temperature while providing a high-capacity heat sink for the desired steady transmission of thermal energy from the filament through the gas to the tube wall. Frequently, the cell output can be increased by replacing the heated filaments with thermistors, which have a very high temperature coefficient of resistivity.

3. Noise and Drift

Noise and drift are frequently encountered problems with thermal-conductivity cells. Noise is a short pulsating change in the output voltage. Noise can be caused by disturbances in the pneumatic connections (e.g., leaks, pressure fluctuation), by flowrate fluctuations, or by electrical disturbances (e.g., fluctuating input voltage or line frequency changes), vibration, shock, inadequate shielding, and grounding.

Drift is a slowly increasing or decreasing output voltage. Drift is caused by changes in gas flowrate and pressure and by operation away from thermal equilibrium. Changes in ambient temperature because of drafts, sunlight, or nearby ovens or furnaces can be overcome by enclosing the metal block in a fully insulated, thermostatted enclosure.

4. Calibration

When functioning in accordance with its theoretical design, the thermal-conductivity cell makes a continual analysis of the composition difference between the reference gas and the sample gas. To obtain a meaningful quantitative output from the cell, the instrument must be calibrated with at least one gas sample of known composition. Theoretical calibrations based on thermal-conductivity data are not considered accurate enough because of the complex relationship between gas mixtures and their associated thermal conductivities.⁶ To establish the calibration, standard gas mixtures (checked by chemical analysis) can be passed through the sample side of the thermal-conductivity cell. For a given flowrate through the cell, a linear proportion may be set up using the output from the known sample as a standard. The reference gas used must be of the same quality and flowrate during standardization and during analysis.

The reference gas in a cell is usually the unchanging component of the process-gas stream against which a change in concentration of a key component in the process stream is referred. Once a cell is calibrated for a particular process gas, the concentration of one or more of the key components in that gas can be continuously determined. The cell is calibrated by using standard gas mixtures of known composition. Initially, several standard gas mixtures, which cover the expected concentration range of the key component in the process gas, are required to establish whether the cell output is linear with respect to concentration of the key component. If the cell output is linear, a single standard gas mixture is sufficient to check the calibration once the cell is operational. If the cell output is nonlinear, several standard gas mixtures may be required for calibration.

The reference gas depends upon the particular process application. For instance, if the key component is hydrogen, a separate, independent supply of nitrogen can be used as the reference gas. When the key component is removed or replaced from the process stream, the reference gas can be the unchanging portion of the process gas. In any case, the reference gas used during calibration of the cell must be the same as that used in the actual process application.

III. APPLICATION TO FLUORIDE-VOLATILITY PROCESSES

Recent application of thermal-conductivity methods to the measurement of reactant concentrations has resulted in an excellent method of analyzing the efficiency of processes under development for the reprocessing of uranium reactor fuel. Process flowsheets applicable to low-enrichment UO_2 - PuO_2 fuel and high-enrichment alloy fuels are shown in Figs. 3 and 4,

respectively. The gases encountered with each type of fuel during any processing step are listed in Table I. Selected physical properties of these gases are listed in Table II.

108-8751 Rev. 1

Fig. 3. Fluid-bed Fluoride-volatility Process Flowsheet for Low-enrichment $\text{UO}_2\text{-PuO}_2$ Fuel

108-8268 Rev. 2

Fig. 4. Fluid-bed Fluoride-volatility Process Flow-sheet for High-enrichment Alloy Fuels

TABLE I. Gases Encountered in Fluid-bed Fluoride-volatility Reprocessing of Spent Reactor Fuel

Diluent Gas: Nitrogen

A. High-enrichment Alloy Fuels

Fuel	Separation (Decladding)	Fluorination	
		With HF	With Fluorine
U-Zr	H ₂ , HCl, ZrCl ₄	HF, O ₂	UF ₆ , F ₂
U-Al	H ₂ , HCl, AlCl ₃ , Al ₂ Cl ₆	HF, O ₂	UF ₆ , F ₂
UO ₂ -SS Cermet	HF, O ₂	-	UF ₆ , O ₂ , F ₂
UO ₂ -Graphite Matrix	CO ₂ , O ₂	-	UF ₆ , O ₂ , F ₂

B. Low-enrichment UO₂-PuO₂ Fuels

Cladding Material	Decladding Step	Fluorination with Fluorine	Thermal Decomposition	Conversion of Hexafluorides to Oxides
Zircaloy	H ₂ , HCl, ZrCl ₄	PuF ₆ , UF ₆ , O ₂ , F ₂	PuF ₆ , UF ₆ , F ₂	PuF ₆ , UF ₆ , HF, H ₂ , H ₂ O, O ₂
Stainless Steel	HF, O ₂			

TABLE II. Selected Physical Properties⁷⁻⁹ of Gases Encountered in Fluid-bed Fluoride-volatility Reprocessing of Spent Reactor Fuel.

Gas	Molecular Weight	Boiling Point, °R	Molal Heat Capacity at Constant Pressure, Btu/(lb mole)(°R)	Thermal Conductivity at 100°F, Btu/(hr)(ft)(°F)	Ratio of Thermal Conductivity of Nitrogen to Thermal Conductivity of Gas
UF ₆	352.1	593.9 ^a	31.0	0.004092	3.8
Cl ₂	70.9	429.6	8.12	0.0053	2.9
HCl	36.5	338.7	6.96	0.0085	1.8
O ₂	32.0	162.2	7.02	0.01595	0.972
F ₂	38.0	155.0	7.52	0.0160	0.969
N ₂	28.0	139.1	6.96	0.0155	1.0
H ₂ O	18.0	672.0	8.02	0.0108	1.505
H ₂	2.0	36.8	6.9	0.111	0.14

^aSublimation point.

The molecular weights of the gases cover a relatively wide range with a corresponding spread in the range of thermal conductivities. For the extreme values of molecular weight, 352 for UF₆ and 2.0 for hydrogen, the corresponding thermal conductivities are 0.004092 and 0.111 Btu/(hr)(ft)(°F). Since nitrogen is used both as a reference gas and as a process diluent gas, the ratio of thermal conductivities of nitrogen to those of the other gases is also of interest. These ratios, which range from 0.14 for nitrogen-hydrogen to 3.8 for nitrogen-UF₆, are also listed in Table II.

As shown in Table I, gas streams in the fluid-bed fluoride-volatility process may contain as many as seven components.* Hence the

*To simplify the discussion, volatile fission-product fluorides have been omitted from Table I.

thermal-conductivity method cannot be used directly and the concentration of the desired key component must be altered between the reference and sample sides of the thermal-conductivity cell before an analysis can be obtained.

A. Analysis of Ternary Gas Mixtures

Thermal-conductivity analyses applied to two ternary gas mixtures of process interest are illustrated in Figs. 5 and 6. In each case, a net change in thermal conductivity of the gas mixture across the legs of the Wheatstone Bridge provides an accurate analysis for a single component in the mixture. For a gas mixture such as water vapor, hydrogen chloride, and nitrogen, the thermal conductivities of the individual components differ sufficiently so that the removal of one component between the reference and sample sides of the cell suffices for a thermal-conductivity analysis as shown in Fig. 5. Water vapor is determined in Cell 1, hydrogen chloride is determined in Cell 2, and nitrogen is obtained by difference. For a gas mixture containing oxygen, nitrogen, and fluorine, removal of one of the components is not only difficult but also not effective since thermal conductivities of the individual gases differ less than 5% at the temperatures and pressures of interest. With such a mixture, the principle of substitution¹⁰ is effective, as illustrated in Fig. 6. The quantitative substitution of fluorine with chlorine provides a component in the gas stream with a thermal conductivity one-third that of oxygen and nitrogen. Therefore, by suitable calibration of the cell, a continuous fluorine analysis is available. By making use of the paramagnetic properties of oxygen, oxygen can also be determined by a method similar to the thermal-conductivity analysis.¹¹ Uranium hexafluoride, the additional component shown in Fig. 6, can also be measured by thermal-conductivity methods since UF_6 can be removed from the gas by condensation and/or adsorption on sodium fluoride at 100°C .

Fig. 5. Thermal-conductivity Analysis of a Ternary Gas Mixture by Removal of Components.

Fig. 6. Thermal-conductivity Analysis of a Ternary Gas Mixture by Substitution of One Gas for Another

B. Analysis of a Gas Mixture for Hydrogen

Thermal-conductivity analysis, as used for measuring the concentration of hydrogen in the off-gas from a reaction involving hydrogen chloride and either uranium-zirconium or uranium-aluminum alloy fuels, is illustrated in Fig. 7. Effluent gas from the reactor is initially passed through a process scrubber to remove the volatile chlorides: HCl , ZrCl_4 , and AlCl_3 . The off-gas sample then passes through a moisture trap and a series of three 2-in.-diam, 12-in.-high brass tubes, which contain granular Ascarite,* sodium hydroxide pellets, and anhydrous calcium chloride, respectively, for complete drying and further purification of the sample gas before it is passed to the thermal-conductivity cell. The reference gas to the thermal-conductivity cell is supplied from an external source.

Fig. 7

Thermal-conductivity Apparatus for Measuring Hydrogen in the Off-gas from a Fluid-bed Hydrochlorinator

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IV. CHARACTERISTICS OF THERMAL-CONDUCTIVITY CELLS AND ASSOCIATED COMPONENTS

To obtain quantitative and reproducible data on gas compositions using the thermal-conductivity cells, the numerical magnitudes of the cell-system characteristics must be known accurately. The numerical values, however, depend to a great extent on the cell dimensions, the type of filaments, the filament resistances, and the operating conditions of the system. Hence, for each installation, these should be determined separately. Typical values from one of the thermal-conductivity cell systems used at Argonne National Laboratory are discussed below.

*Trade name for asbestos coated with sodium hydroxide.

A. Thermal-conductivity Cells Used in Fluoride-volatility Development Studies

Fig. 8. Gow-Mac Thermal Conductivity Cell, Model 9454 (30-S Geometry)

In development studies of the fluid-bed fluoride-volatility process, continuous analysis of process effluent gases has been carried out with Gow-Mac* Model 9454 thermal-conductivity cells (30-S geometry). Each cell contained four (or eight) heated filaments in a 2 by 2 by $1\frac{7}{8}$ -in. metal block. The block was heated above ambient temperature in an insulated, thermostatted enclosure, which ensured uniform temperatures in the metal surrounding the filaments. The cell is a fast-response, diffusion-type cell producing an output relatively independent of sample flowrate from 50 to 1000 cc/min. The cell geometry and electrical wiring diagram are shown in Figs. 8 and 9, respectively. The gas volume of each internal passage, with its filament cavities and two $1/8$ -in.-ID, $7/8$ -in.-long nipples, is 4.65 cc.

The advertised speed of response is 10 sec for 150-mA bridge current and 750 cc/min flow through sample and reference sides for 66% of full deflection on changeover by solenoid valve from 100% air to 100% argon.

Cell characteristics of interest for the fluid-bed fluoride-volatility process were determined in conjunction with pilot-plant studies¹² of the fluorination of uranium dioxide pellets with elemental fluorine. Here the progress of reaction could be monitored by continuous analysis for fluorine and uranium hexafluoride in the reactor effluent gas, which consisted of fluorine, uranium hexafluoride, oxygen and nitrogen.

1. Experimental System Used to Determine Operating Characteristics

The experimental system used to test the operating characteristics of the thermal-conductivity cells is shown

Fig. 9. Wiring Diagram for Gow-Mac Thermal-conductivity Cell, Model 9454, and Power Supply, Model 9999C

*Gow-Mac Instrument Company, Madison, N. J.

schematically in Fig. 10. The system consisted of two thermal-conductivity cells in series: one for uranium hexafluoride analysis, and one for fluorine analysis. Sodium fluoride at 100°C was used for the removal of uranium hexafluoride between the reference and sample sides of Cell 1; similarly, sodium chloride at ambient temperature was used to substitute chlorine for fluorine between the reference and sample sides of Cell 2.

Fig. 10. Thermal-conductivity Cell System for Continuous Measurement of Fluorine and Uranium Hexafluoride in Reactor Off-gas

Fluorinator effluent gas or standard calibration gases were introduced into the system at flowrates in the range 50-200 cc/min. The concentration and pressure of the fluorinator effluent gas were known to fluctuate; therefore, provision was made to introduce a step change in these parameters to appropriate points in the system (as shown in Fig. 10). The step changes were used to determine time constants and transportation lags in the cells, associated piping, and traps. The magnitude of these lags was required to determine whether the speed of response of the measuring system was fast enough to respond to rapid changes in the fluorine concentration and if necessary, to modify the measuring system for faster response so that the cell output signal could be used for automatic process control.

The cell power supplies were equipped with zero and sensitivity controls, which were used to adjust the intercept and slope, respectively, of the curves of cell output voltage versus concentration. Bridge current from the power supplies was accurately metered by means of an added 50-150-mA ammeter and resistance in series with the current-regulating potentiometer. The cell output voltage was attenuated to the range 0-3 mV and recorded on a 12-point recorder, six points being allotted to each cell. Zero and span controls on the recorder were adjusted to read 90% of full scale at 3-mV cell output.

2. Standard Gas Mixtures

Fluorine-nitrogen mixtures containing 1.3, 5.1, and 13.6% fluorine were produced by PVT methods and stored at pressures of 60 psig or less in empty 6-lb fluorine cylinders equipped with regulators. Fluorine concentrations were determined by analysis using mercury in a calibrated volume.¹² Similarly, uranium hexafluoride-nitrogen mixtures containing 1.4, 3.9, and 7.8% UF_6 were prepared and analyzed by wet chemical methods.

3. Capacity Tests of Solid Adsorbents

It was desired to know the actual working capacity of the sodium chloride trap, as compared to its stoichiometric replacement value for fluorine. The capacity of the trap was determined by passing a known concentration of fluorine in nitrogen through the cell system and continuously recording the cell output. Breakthrough of the trap was defined as the point where the cell output began to decrease from a constant value. The extent of reaction was calculated from the volumetric flowrate and composition of the test gas and was checked by the weight change of the sodium chloride. The capacity of the trap (calculated from the flowrate) was based on the time for breakthrough. The results of several capacity tests for a trap containing 178 g of NaCl are shown in Table III.

TABLE III. Results of Capacity Tests of Sodium Chloride Trap

Charge to trap: 178 g of reagent-grade NaCl

Test	Fluorine, %	Flowrate, cc/min	Breakthrough ^a Time, hr	Trap Capacity, g of F_2 per g of NaCl
1	13.6 ^b	400	9.45	0.32
2	18.9	400	6.88	0.30
3	19.6	400	6.80	0.32

^aBreakthrough is defined as the time of initial deviation of the cell output from a constant value.

^bThe 13.6% fluorine gas mixture was used up during the test; the test was continued with 18.9% fluorine, and breakthrough time was prorated for the original test-gas composition.

The gas mixtures used in these tests contained about 19% fluorine in nitrogen. Both the fluorine concentration and the flowrate were higher than would normally be expected during actual operation of the measuring system so that a test of trap capacity could be completed in one day; consequently, the sodium chloride trap was heated to a higher temperature than normal, because of the evolution of heat in the replacement reaction.

This problem was accentuated by the fact that, as indicated by the temperature pattern along the length of the cylinder, at a given time most of the reaction took place along a fairly well-defined relatively small zone. This resulted in strong local heating rather than mild general heating. The trap reached an estimated temperature of 80 or 90°C. This is below the temperature at which chlorine-fluorine compounds would be expected to form. Nevertheless, to prevent their possible formation, a fan was used in Tests 2 and 3 to cool the NaCl trap.

The average capacity of the sodium chloride trap was determined to be 0.31 g of fluorine per gram of NaCl, which is 96% of the stoichiometric replacement value. If a flowrate of 100 cc/min is assumed for a sample gas containing an average of 8% fluorine, a trap containing 178 g of NaCl would be expected to operate efficiently for 64 hr.

Although no specific experiments were carried out to determine the capacity of the sodium fluoride traps for UF_6 , experience indicated that this type trap required replacement more often than the sodium chloride trap. Saturation of a sodium fluoride trap was characterized by a steady decrease in the recorded output of the UF_6 cell. It was estimated that saturation of the trap occurred at a loading of 0.3 g of UF_6 per gram of NaF (0.2 g of uranium per gram of NaF). This loading represents about 43% of effective capacity, as calculated from data obtained by Cathers *et al.*¹⁴ with the same size sodium fluoride pellets (1/8-in. diameter by 1/8-in. height). A reason for the lower loading obtained in the present work may be that Cathers *et al.* used a static system, whereas in the present case the UF_6 flows through the bed with a relatively short residence time for a given UF_6 molecule.

4. Drift in Power Supply and Thermal-conductivity Cell

The drift properties of the thermal-conductivity cell and associated power supply were observed over long periods of time, i.e., a minimum of 24 hr. The power supply drifted as much as 5% (5 mA in 100 mA) in a 16-hr period. Since the cell output voltage is proportional to the square of the bridge current, changes in the output voltage of 10-12% were noted. Furthermore, simply readjusting the bridge current back to its original value did not fully compensate for the drift. When a constant output of the power supply was maintained, the drift in the components other than the power supply was less than 1% in 24 hr.

All types of drift appeared to be minimized after the cell thermostat and current supply had been allowed to equilibrate for 2 or 3 days. Because of these observations, the following operating procedures were adopted: To eliminate warmup effects, the cell heaters were run continuously and power supplies were switched on 12-24 hr before use. Also,

before use, the intercept and slope of the calibration curve were checked by readjusting the zero control with nitrogen flowing through the cell and readjusting the sensitivity control with a calibration gas flowing through the cell.

5. Response Time of Measuring System

An analysis was made of the speed of response of the thermal-conductivity cell system to changes in fluorine and uranium hexafluoride concentrations in the fluorinator effluent gas. The time lags in the system consisted of time constants* and transport lags. The time constants were measured by effecting step changes in the gas concentration introduced at Point A in Fig. 10. An arrangement of three-way valves at Points A and B allowed the step change to be introduced with a minimum pressure surge. Time constants and transport lags were as follows:

Time constant of NaCl trap	15-17 sec
Time constant of NaF trap	4 sec
Transport lag of tubing in thermal-conductivity cell systems	2.25 min

Alternating step changes between 1.4% UF_6 and 5.1% fluorine were introduced to the cell system at Point B. The transport lag was measured as the time required for the first change in the output signal to be recorded, and the total response time was measured as the time required for the recorder to register 95% of the total change. Transport lags and response times for both the UF_6 cell and the fluorine cell are detailed in Table IV. The results indicate that for both cells the response to a decrease in concentration of the measured gas is more rapid than the response to an increase. For instance, in the step changes from UF_6 to fluorine (decreasing UF_6 concentration), the response time of the UF_6 cell is 1.01 min; in the step changes from fluorine to UF_6 (increasing UF_6 concentration), the response time of this cell is 1.35 min. Likewise, the average response time of the fluorine cell to decreasing concentration is 3.47 min and to increasing concentration 3.70 min.

Note that the response time of the measuring system depends upon the system under study.

Short response times may be required if output from the cells is fed back to a controller which regulates reactant flowrates, reactor cooling, or some other operating parameter. With open loop control, i.e., manual control of operating parameters, fast response times may be desirable but not necessarily critical.

*See Appendix for definitions of special terms.

TABLE IV. Response Times for UF_6 and Fluorine Thermal-conductivity Cells^a

Run Conditions:		Flowrate	100 cc/min
		Pressure	3 psig
		Gas mixtures	1.4% UF ₆ -N ₂ (0% F ₂) 5.1% F ₂ -N ₂ (0% UF ₆)
Cell Conditions			
		Bridge Current, mA	Cell Block Temperature, °C
UF ₆ Cell		55	32
Fluorine Cell		150	60

UF ₆ Cell		Fluorine Cell		
Test	Transport Lag, min	Total Response Time, min	Transport Lag, min	Total Response Time, min
Step Change: UF ₆ -N ₂ to F ₂ -N ₂				
1	0.21	0.90	2.70	4.41 ^b
3	0.20	1.10	1.95	3.58
5	0.20	1.00	2.10	3.80
7	0.20	1.05	2.25	3.72
Average	0.20	1.01	2.25	3.70
Step Change: F ₂ -N ₂ to UF ₆ -N ₂				
2	0.30	1.60	2.10	3.55
4	0.30	1.25	2.00	3.42
6	0.25	1.20	2.00	3.45
Average	0.28	1.35	2.03	3.47

^aThe thermal-conductivity cell system shown in Fig. 10 was used in these tests.

^bApproximate time.

In the system shown in Fig. 10, total response time would include an additional transport lag of 0.7 min for passage of the gas sample from the reactor effluent line to Point B; therefore, the total response time for the fluorine cell to increased concentration (4.4 min) includes 2.9 min of transport lag and time constants. The transport lag of the cell-system tubing is proportional to tubing length and inversely proportional to gas velocity. Minimization of tubing length could be facilitated by moving

the cell system physically closer to the reactor and by minimizing the amount of tubing necessary to connect the cells, traps, etc., in the system. The gas velocity may be increased by increasing the volumetric sampling rate or by decreasing the tubing diameter. Decreasing the tubing diameter is preferable in this case since an increased flowrate would also increase the amount of uranium hexafluoride and fluorine to be removed by the NaF adsorber and the NaCl trap. It is estimated that the total transportation lag of the measuring system could be reduced to approximately 0.5 min by replacing the 3/8-in.-OD tubing with 1/8-in.-OD, thick-wall tubing and designing the system for minimum tubing length.

B. Effect of Operating Variables on Cell Calibration

1. Gas Flowrate and Surge Sensitivity

The sensitivity of the fluorine thermal-conductivity cell to changes in internal pressure and sample-gas flowrate was determined by calibrating the measuring system at various pressures and flowrates with fluorine-nitrogen gas mixtures.

The gas flowrate was varied from 50 to 200 cc/min at 100 mA bridge current and 18 psia internal pressure. Calibration remained linear for a given gas flowrate with variable fluorine concentrations; however, the slope of the calibration curve increased 9% between 50 and 200 cc/min, as shown in Fig. 11.

Fig. 11. Effect of Sample-gas Flowrate on Calibration of Fluorine Thermal-conductivity Cell

With a sample-gas flowrate of 100 cc/min and a bridge current of 100 mA, the internal pressure of the cell was varied from 8 to 20 psia. (The pressure was uniform throughout the tubing train between the needle valves shown in Fig. 10.) At positive pressures of 16 to 20 psia, the cell

output remained linear with variable fluorine concentrations as shown in Fig. 12. However, at negative pressures of 8-12 psia, cell output became nonlinear as shown in Fig. 13.

Fig. 12

Effect of Steady-state Internal Cell Pressure on Calibration of Fluorine Thermal-conductivity Cell for Positive Pressures

Fig. 13

Effect of Steady-state Internal Cell Pressure on Calibration of Fluorine Thermal-conductivity Cell for Negative Pressures

Surge sensitivity* was determined to be 1% of cell output per psi surge at pressures of 17 psia and above. At 16 psia and below, surge sensitivity was as high as 20%. These results are shown in Fig. 14.

From the above observations, the cell output was found to be insensitive to steady-state pressure changes and nonsteady-state pressure surges at positive gauge pressures of 17-20 psia. At lower pressures, however, steady-state calibration became nonlinear and the surge sensitivity increased. Thus, if a linear output from the thermal-conductivity cell is required, cell pressure must be kept at 17 psia or above.

*Defined in Appendix.

$$\text{SURGE SENSITIVITY} = 100 \times \left(\frac{\text{MILLIVOLT OUTPUT CHANGE DUE TO SURGE}}{\text{MILLIVOLT OUTPUT BEFORE SURGE}} \right) / \text{PSI SURGE}$$

Fig. 14. Pressure-surge Sensitivity of Fluorine Thermal-conductivity Cell as a Function of Steady-state Pressure

55 mA. With this bridge current, the calibration was slightly nonlinear but could be maintained within 5% of the calibration at 150 mA by suitable adjustment of the sensitivity control.

Operation of the thermal-conductivity cell at 35-mA bridge current resulted in a maximum output voltage only 20% of the maximum obtained at 55 mA. In these tests, the 13.6% fluorine in nitrogen and the 7.8% UF_6 in nitrogen gas mixtures were used and the sensitivity control was set at the maximum value (i.e., no attenuation of the output signal; see Fig. 9). With the low-level output voltage, noise reached values of 25% and

2. Effect of Bridge Current on Cell Output

Variation of cell output voltage as a function of bridge current over the range 100-150 mA is shown in Fig. 15. Fluorine-nitrogen standard gas mixtures and a constant setting of the sensitivity control were used for these measurements. The calibration remained linear, although the slope increased by a factor of 5 from the lowest to the highest bridge current. However, with any bridge current in the above range, the slope could be made to nearly coincide with the 150-mA calibration by adjustment of the sensitivity control, as shown in Fig. 16. Also shown in Fig. 16 is the calibration for a bridge current of

Fig. 15

Effect of Cell (Bridge) Current on Calibration of Fluorine Thermal-conductivity Cell

Fig. 16

Effect of Power-supply Sensitivity Setting on Calibration of the Fluorine Thermal-conductivity Cell. (Sensitivity setting on power supply is varied with bridge current to cause a constant chart reading at highest fluorine concentration, 13.6 v/o.)

more of the output signal. It was concluded that the minimum bridge current required for a suitable cell output signal was 55 mA.

C. Cell Filament Temperatures

The filament temperature as a function of bridge current was determined from the electrical resistance of the nickel filament. A volt-ohm-milliammeter was used to measure filament resistance. The initial resistance measurement was made at a known temperature, that of the cell body in the thermostatted enclosure. Filament temperatures were then obtained by relating the measured resistance to the temperature coefficient of resistance for nickel.¹⁵

Filament temperatures as a function of bridge current are shown in Fig. 17 for cell-body temperatures of 34 and 60°C. Typical filament temperatures are 195°C with cell-body temperature of 34°C and 55 mA current, and 390°C with the cell body at 60°C and 150 mA current. A minimum cell-body temperature of 50°C may be required because of the presence of condensibles in the effluent gas stream from a fluorination reactor (e.g., UF_6 , PuF_6). The lowest bridge current was determined to be 55 mA (as mentioned in Section IV.B.2). Consequently, from Fig. 17 it may be seen that the minimum operable filament temperature is approximately 195°C.

Fig. 17. Filament Temperature of the Uranium Hexafluoride Thermal-conductivity Cell as a Function of Bridge Current

At this temperature, a significant amount of plutonium hexafluoride decomposition¹³ to plutonium tetrafluoride may occur on the filaments, changing the cell calibrations. If thermal-conductivity cells are used in a plutonium hexafluoride environment, accumulated plutonium tetrafluoride may have to be removed periodically from the filaments.

D. Cell Repair and Maintenance

In general, the only repair or maintenance required for the thermal-conductivity cell and power supplies has been the occasional replacement of the hot-wire filaments. Since the filaments are added to the bridge circuit in matched pairs of two, at least two filaments must be added each time a filament fails. Because of the highly corrosive environments in the fluidized-bed fluoride-volatility process, replacement of all the filaments in a cell represents an efficient and economical standard practice.

In bench-top or nonradioactive areas, the filaments are easily replaced. In a plutonium glovebox, the thermostatted enclosure has been taken apart, the filaments replaced, and the unit reassembled and checked out in 4 hr.

V. OPERATING EXPERIENCE

In the development of the fluid-bed fluoride-volatility process, thermal-conductivity cells have been installed on an operational basis in six experimental units incorporating 1.5-, 2-, 3-, and 6-in.-diam fluid-bed reactors. Simulated fuels containing uranium were processed in all these units. Two of the systems were used to process fuels containing uranium and plutonium. During processing, various process gas streams^{12,16,17} have been monitored continuously for hydrogen, hydrogen chloride, fluorine, or uranium hexafluoride.

A. Processing of Low-enrichment Ceramic Fuels

In the processing of low-enrichment fuels with fluorine, the major application for off-gas analysis by thermal-conductivity measurement occurs during fluorination of the major constituent, UO_2 , to form the volatile UF_6 . Intermediate products formed during the fluorination include U_3O_8 , UO_2F_2 , and UF_4 .

The production rates for UF_6 and the response of thermal-conductivity cells to fluorine and UF_6 in the reactor effluent gas for a typical experiment (Run 76,¹²) are shown in Figs. 18-20. In this experiment, 7 lb of UO_2 pellets, clad in perforated stainless steel tubes, were processed by oxidation in a lower zone and by fluorination in an upper zone of a 3-in.-diam fluid-bed reactor. Figure 19 shows the actual response of the thermal-conductivity cells during the run. Average UF_6 concentrations in

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Fig. 18. Production Rate for Uranium Hexafluoride in a 3-in.-diam Fluid-bed Reactor

the off-gas over half-hour intervals were calculated from the reactor input data and the UF_6 collection rates (Fig. 18). The average concentrations thus obtained are compared with averaged data from the thermal-conductivity cell as shown in Fig. 20. Data from the thermal-conductivity measurements indicate an average UF_6 concentration about 12% higher than calculated values. The several uncertainties in the calculated average concentrations include: (1) the amounts of U_3O_8 , UO_2F_2 , and UF_4 formation, (2) variations in the gas flowthrough the thermal-conductivity system

caused by blowback of filters and bubbling of the fluidized bed, and (3) incomplete analysis of the off-gas; i.e., only two of the four components, fluorine, oxygen, nitrogen and UF_6 , were determined.

Fig. 19
Fluorine and Uranium Hexafluoride in Reactor Off-gas from a 3-in.-diam Fluid-bed Reactor

Fig. 20

Uranium Hexafluoride in Reactor Off-gas from Thermal-conductivity Measurements and from Experimental Data

An independent analysis of the fluorine in the off-gas was not available for comparison with the thermal-conductivity data in Fig. 19. Additionally, the fluorine concentration could not be calculated from the gas input and UF_6 collection data because more than half the effluent gas was recycled back to the reactor. However, an idea of the quantitative accuracy of the thermal-conductivity cell data may be obtained by comparing the cumulative fluorine utilization calculated from input-output data with that calculated from the cell data. After 6 hr of operation, 95.6% of the available uranium had been converted to the hexafluoride. Fluorine utilization during this period, based on hexafluoride collection and cell data, was 90%. This result compared favorably with a utilization of 88% calculated from the total fluorine input and total UF_6 collection in the run.

Since the thermal-conductivity measurements appear to be in reasonable agreement with calculated values, the measurements can be used to follow complex chemical reactions to determine when intermediate solid products, which are not directly detectable, are being formed. For example, in Fig. 19 the initial fluorine concentration is 0%, and double peaks in the uranium hexafluoride concentration occur without a concurrent variation in the fluorine concentration at about 6.0 hr of operation. These effects may indicate that utilization of fluorine is complete during early portions of a run because fluorine is consumed not only by formation of UF_6 product, but also by formation of intermediate uranium fluorides and oxyfluorides. The peaks in UF_6 concentration are due to fluorination of the intermediate compounds. These peaks are too short-lived to show up in the average UF_6 rates presented in Fig. 18. Similarly, fluorine concentration would not be expected to fluctuate as rapidly as UF_6 concentration because fluorine was continuously added to the reactor from the fluorine feed line and from recycle (0.65 cfm) of the fluorinator off-gas.

Figure 21 shows fluorine concentration in a similar 3-in.-diam fluid-bed system for the same kind of two-zone oxidation-fluorination experiment but without recycled effluent gas.¹⁸ Here the results obtained from the thermal-conductivity analysis are compared with calculated values based on fluorine input and hexafluoride production rate. The good agreement indicates that little, if any, accumulation of intermediate uranium fluorides occurred during the run.

In an installation containing a 2-in.-diam fluid-bed reactor, the thermal-conductivity cell provided information on the rate of formation of UF_6 and fluorine utilization during fluorination of uranium from UO_2 - PuO_2 -fission product pellets.¹⁹ Two types of experiments were conducted in the reactor: (1) the two-zone method of simultaneously oxidizing and fluorinating the pellets, and (2) the oxidation and fluorination of the pellets in separate successive steps. Table V compares the experimental data and the results calculated from the thermal-conductivity measurements for

both types of experiments. The calculated results are higher than the experimental data by 3-6%. This result is expected because the experimental data are based on collected hexafluoride product, and the thermal-conductivity results are based upon the measurement of total fluorine consumed in the reactor, which also includes the fluorine used in forming solid intermediate uranium and plutonium fluorides, fission-product fluorides, and aluminum fluoride in the alumina bed.

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Fig. 21. Fluorine in Reactor Off-gas from a 3-in.-diam Fluid-bed Reactor

TABLE V. Experimental and Calculated Results from a 2-in.-diam Fluid-bed Reactor Contained in a Plutonium Glovebox

	Two-zone Oxidation- Fluorination	Fluorination of Oxidized Pellets
<u>UF₆ Production, lb UF₆/(hr)(sq ft)</u>		
Experimental: Based on weight of hexafluoride collected	22.0	38.5
Calculated: Based on off-gas thermal-conductivity measurements	22.7	40.8
Deviation from experimental value, %	-3.2	-6.0
<u>Fluorine Utilization to form UF₆</u>		
Experimental: Based on hexafluoride collection and fluorine input	44.9	38.3
Calculated: Based on off-gas thermal-conductivity measurements	46.2	40.1
Deviation from experimental value, %	-2.9	-4.7

B. Processing of High-enrichment Alloy Fuels

In the processing of high-enrichment uranium-Zircaloy alloy and uranium-aluminum alloy fuels, both hydrochlorination and fluorination reactions are the areas of high interest for application of thermal-conductivity analysis. During hydrochlorination, the concentration of hydrogen product in nitrogen (off-gas stream) has been measured by thermal-conductivity cells containing glass-bead thermistors in bench-scale development work,¹⁶ and by thermal-conductivity cells containing nickel filaments in engineering-scale development work.¹⁷ Further, the concentrations of hydrogen chloride, fluorine, and uranium hexafluoride in nitrogen have been measured by thermal-conductivity cells containing nickel filaments.

VI. CONCLUSIONS

In the development of processing techniques for nuclear fuels by fluid-bed fluoride-volatility methods, knowledge of the progress of chemical reaction is of vital interest. A useful and practical method of monitoring the volatility reactions is by the continuous thermal-conductivity analysis of the gaseous reaction products evolved from the fluid-bed reactors. This analysis has been used to obtain data on UF_6 production rates, on the extent of chemical reactions forming solid intermediates, and on the utilization of gaseous reactants. With respect to the utilization of reactants, the thermal-conductivity method of continuous off-gas analysis appears to be most useful during reaction of the major constituents of a fuel when a relatively expensive reactant must be economically utilized, e.g., the utilization of fluorine during the fluorination of uranium from low-enrichment ceramic fuels. Additionally, off-gas analysis by thermal-conductivity methods offers much promise as a method for automatic process control of the fluorination reactor. Such a control system has been successfully demonstrated²⁰ in an alpha facility in which the output from the thermal-conductivity cell was used to control fluorine feed to the reactor.

APPENDIX

Glossary of Special Terms

Bridge Current or Cell Current: Total current from power supply to thermal-conductivity cell. This current is split, and half goes to each side of the Wheatstone Bridge in the thermal-conductivity cell.

Cell Voltage or Output: The imbalance voltage in the cell Wheatstone Bridge, which is the electrical output of a cell due to difference in thermal conductivity of the sample and reference gases.

Drift: A gradual change in calibration over a long period of time.

Gas Flowrate: The volumetric flowrate of gas flowing through the thermal-conductivity cell system.

Internal Pressure: Pressure in thermal-conductivity cell-system tubing train between the needle valves shown in Fig. 10.

Measuring System or Cell System: The entire system consisting of two thermal-conductivity cells, power supplies, traps, tubing, valves, etc., from the gas sampling tap-off (downstream of the reactor or condenser) to the vacuum line.

Noise: A random variation in cell-voltage output over a short period of time (~1-2 min).

Response Time: The total time lag from the time of a change in gas concentration in the fluorinator off-gas to the time 95% of this change is recorded.

Sensitivity Control: A control on the thermal-conductivity cell power supply, which adjusts the slope of the curve of the cell output voltage versus gas concentration.

Speed of Response: The time required for the output of a thermal-conductivity cell to respond to changes in gas concentration in the off-gas, as measured from the sampling tap-off to the recorder.

Surge: A change in the internal pressure of the thermal-conductivity cell system. For testing purposes, a surge lasting 0.5-2 min was induced by use of the needle valves shown in Fig. 10.

Surge Sensitivity: A ratio used to quantitatively characterize the changes in cell output due to surges in internal pressure and defined as

$$100\% \times \frac{\text{change in chart reading due to surge}}{\text{chart reading before surge}} / \text{psi surge.}$$

Thermal-conductivity Cell: A single Gow-Mac thermal-conductivity cell, together with its heater, insulation, and thermostat.

Time Constant: A quantity defined by the differential equation

$$y(t) = \frac{Kx(t)}{Ts + 1},$$

where $y(t)$ and $x(t)$ are the output and input signals, respectively, as functions of time, K is the steady-state proportional gain (slope of steady-state calibration curve), T is the time constant, and s is the time differential or Laplace transform operator.

In terms of response to a step change from a value $x = x_0$ to $x = 0$, the time constant is used in the expression

$$y(t) = x_0 \exp(t/T),$$

where t is time.

Zero Control: A control on the cell power supply which adjusts the intercept of the curve of output voltage versus concentration.

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