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A THERMOBALANCE FOR HIGH PRESSURE PROCESS STUDIES

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ABSTRACT

A DuPont 950 TG has been modified to permit operation at up to 30 atm, 1100°C, with corrosive atmospheres, and steam partial pressures up to 20 atm.

The major areas of instrument development included:

weight and temperature measurement at high pressures in a dynamic flow system;

modification of a TG to accept corrosive gas atmospheres containing high partial pressures of steam;

design of a pressure balanced flow system for safe introduction of corrosive gas atmospheres;

design of a working steam generation system for low flows.

Process studies illustrating the utility of the high presure thermobalance include the cyclic CO_2-acceptor reaction for half-calcined dolomite

$$[CaCO_3 + MgO] = [CaO + MgO] + CO_2$$

and the cyclic H_2S absorption and regeneration reaction for half-calcined dolomite

$$[CaCO_3 + MgO] + H_2S = [CaO + MgO] + H_2O + CO_2$$

INTRODUCTION

With the advent of the recent energy crisis, new technologies are being developed to improve the utilization of our fossil fuel resources. The initial commercialization of these technologies will require huge sums of capital, most likely in the form of government supported financing. The costs of building pilot plants of reasonable size are, however rapidly approaching the cost of demonstration plants themselves. We are also learning very quickly that the goals of process development hinge more strongly on questions of system operability than on any other factors, such as yields and throughput. Unfortunately, system operability can really only be demonstrated on a scale approaching commercial size. The expense of pilot plant programs and their long lead times to implementation demand a viable and more realistic bench scale program to provide some early fundamental answers. There is therefore a growing demand for development of bench scale instruments capable of operating at conditions which more closely simulate the particular processes.

The development of commercial thermobalances has traditionally been oriented toward the polymer industry, where questions of product stability, characterization and quality are of prime importance. The demands made on such instruments are in general not too severe. They are designed to operate in vacuum to atmospheric pressures, cryogenic temperatures to near 800°C using inert or mildly reactive gas atmospheres.

The need to develop an instrument capable of handling highly reactive and corrosive gas atmospheres at high pressures and temperatures arose from our efforts to study sulfur acceptor chemistries. In particular an experimental program was initiated to study the feasibility of using calcined dolomites for high temperature sulfur removal from fuel gases arising from the pressure gasification of coal. The scope of the research includes the quantitative kinetic evaluation of the absorption and regeneration reactions, as well as determining certain qualitative information on optimum process conditions for maintaining high solid reactivities after several cycles. In effect, the thermobalance was called on to do the job of a "micro" pilot plant. The thermobalance must be able to operate at high pressure, high temperature, and in gas environments containing corrosive sulfur species and sometimes high partial pressures of steam.

These requirements were met by a DuPont 950 TG modified to permit operation at pressures up to 30 atm, temperatures to 1100°C, corrosive gas atmospheres, and steam partial pressures up to 20 atm. Its development is described below.

EXPERIMENTAL

Pressure thermobalances

The development of high pressure thermobalances has been a continuing effort over the past two decades. Table 1 summarizes the chronology of these developments as described in the open literature. As yet, no high pressure thermobalances are available commercially.

The earlier units, in general, did not have a dynamic flow system for sweeping the reaction products away from the sample. The first high pressure thermobalance capable of process studies was described by McKewan[4]. This unit and many subsequent units provided for the vertical suspension of the sample in a heated zone from an isolated balance housing which contained a transducer, quartz spring, or torsion assembly. Reaction gas continuously flowed vertically over the sample while purge gas flowed through the upper unheated zone to protect the balance assembly.

In an effort to reduce the size of the pressure assembly and to minimize the need for custom built components, several investigators have developed high pressure apparatus based on the DuPont 950 TG[8,10–13,16]. Figure 1 shows a schematic of the apparatus as provided by DuPont. Close coupling of the furnace and furnace tube to the balance housing is made possible by suspending the sample directly from the balance beam. The horizontal orientation of the furnace tube and gas flows help to reduce convection effects observed in apparatus having a vertical orientation.

TABLE 1

PRESSURIZED THERMOBALANCES

	Balance mechanism	*Orientation*	*Max. pres., (atm)*	*Max. temp., (°C)*	*Flow system*	*Gases*
Rabatin and Card, 1959[1]	torsion	vertical	40	1200	static	CO_2, N_2, CO (O_2, NH_3, H_2S)
Baker, 1962[2]	quartz spring	vertical	300	1300	static	CO_2
Biermann and Hienrichs, 1962[3]	transducer	vertical	70	1000	static	O_2, N_2
McKewan, 1962[4]	quartz spring	vertical	40	1000	dynamic	H_2
Boehlen et al., 1964[5]		vertical	20	500	static	N_2, CO_2, CH_4, C_2H_6
Feldkirchner and Johnson, 1968[6]	transducer	vertical	100	925	dynamic	N_2, H_2, CO, CO_2, CH_4, H_2O
Sasaki et al., 1969[7]		vertical	100	1000	static	
Brown et al., 1971[8]	DuPont	horizontal	20	350	static	N_2
Ho Bae, 1972[9]	transducer	vertical	70	600	dynamic	N_2, air
Williams et al., 1972[10], 1973[11]	DuPont	horizontal	500	500	static	N_2, CO_2
Dobner, 1972	DuPont	horizontal	30	1100	dynamic	N_2, CO_2, O_2, CO, H_2, H_2S, SO_2, H_2O
Keairns, 1972[12], 1973[13]	DuPont	horizontal	40	1100	dynamic	N_2, CO_2, O_2, CO, H_2, H_2S, SO_2, H_2O
Gardner et al., 1974[14]	transducer	vertical			dynamic	H_2, H_2O
Chauhan et al., 1975[15]	transducer	vertical	100	1200	dynamic	H_2, H_2O, He
Tomita et al., 1975[16]	DuPont	horizontal	35	1000	dynamic	H_2

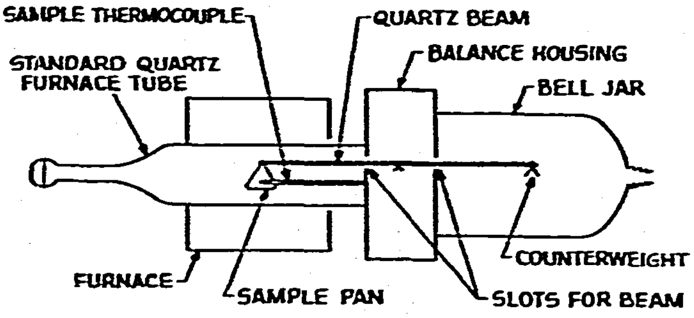


Fig. 1. The DuPont 950 thermogravimetric analyzer.

While the feasibility of pressurizing the DuPont TG was demonstrated by Brown et al.[8] and Williams et al.[10,11], operation in dynamic atmospheres and at temperatures above 500°C had as yet not been established. Our instrument development objectives called for further modification of the DuPont TG to permit operation at temperatures to 1100°C, pressures to 30 atm and corrosive gas environments containing H_2S, SO_2, CO, and high partial pressures of steam. Other research groups have since followed our development and have constructed units having similar capabilities[12,13,16].

Modification of DuPont TG for atmospheric studies

The TG, as provided by DuPont (Figure 1) accepts the reaction gas through an opening in the balance housing which then passes over the sample and exits at the rear of the quartz furnace tube. In this form the DuPont TG is not equipped to handle corrosive gases or steam since either would ruin the balance. The TG, was, accordingly, modified by Ruth as described in refs. 17 and 18. This required redesign of the quartz furnace tube and a baffle to separate the balance and reaction zones. The purpose was two-fold: to keep corrosive reaction gases from the balance mechanism, and to keep purge nitrogen away from the sample, so that the composition of gas in the reaction zone is not affected.

Modification of DuPont TG for high pressure studies

Pressurization was achieved by enclosing the balance and furnace module inside a pressure vessel, as shown in Fig. 2. Designed for 450 psig, the pressure vessel measures approximately 3 ft, long and 10 in. in inside diameter. The unit consists of a horizontal pressure shell on rails to permit easy access to the TG and a fixed bulkhead through which all instrument and flow connections are made. The TG itself rests on a beam extending from the fixed end. Heat generated by the TG is removed by a cooling water jacket surrounding the pressure shell. An 1/8 in. pancake cooling coil located on the face of the balance housing provides additional protection for the balance mechanism.

In principle, the furnace tube as modified by Ruth should also be capable of

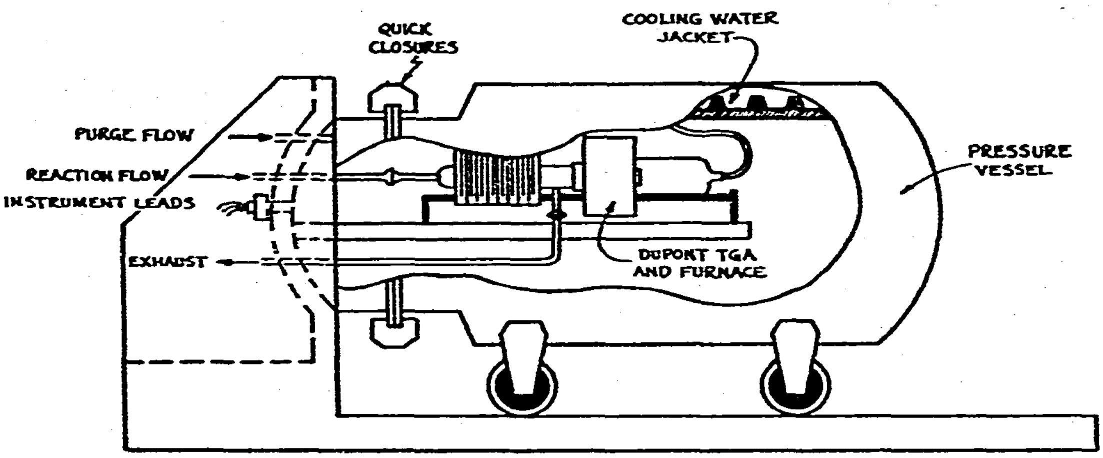


Fig. 2. DuPont TG in high pressure cartridge.

high pressure operation. However, serious problems were encountered when using this configuration in the high pressure unit.

During early shakedown runs of the unit, it was observed that a high pressure (300 psig) the characteristic calcination temperatures of dolomite in one atmosphere of CO_2 appeared to be shifted to higher temperatures by 60 to 100°C. This shift could not be simply explained on any chemical basis. Errors in temperature measurement were therefore suspected, and this was subsequently confirmed by temperature calibrations of the instrument at high pressures using the melting point of aluminum (660°C) and silver (966°C) as standards. This calibration procedure required the construction of aluminum and silver sample pans having the same geometry as the platinum pans used in the experiments. These pans were suspended from the balance beam by tungsten wires. During temperature programming a sharp weight loss would be registered at the melting point of these materials. At atmospheric pressure this calibration procedure showed the sample thermocouple to be satisfactorily accurate to within 10°C. However, at 300 psig the indicated melting points were consistently 60 to 80°C higher than their true values.

The source of these difficulties was quickly identified. In the DuPont TG the sample thermocouple is not in direct contact with the sample but is situated a few millimeters above it (see Fig. 1) and consequently only "sees" the sample temperature. The geometry of the furnace is such that reaction gases entering the furnace tube never approach anything near the furnace wall temperature. The convection effects resulting from the "cold" flowing gases can play havoc with temperature measurement, especially at high pressures, where convection cooling becomes very effective. The fact that the indicated sample temperature was consistently higher than the actual sample temperature at high pressures may reflect a more effective cooling of the sample pan in comparison to the sample thermocouple, the difference owing to their very different geometries.

The "cooling" effect was confirmed by simultaneous measurements of the furnace wall and sample thermocouple readings. At high pressures the sample thermocouple was 100 to 180°C "cooler" than at atmospheric pressure.

A remedy to the troubling convection effects would be to remove the source of temperature inhomogeneities by preheating the incoming reaction gases to sample temperature. This was simply achieved by packing the furnace tube ahead of the sample with 1/8 in. vycor cylinders. This technique, however, met with only partial success. A convection cell was formed between the hot gas inside the heated zone and the cooler gases down-stream of the heated zone. This resulted in unstable temperature readings.

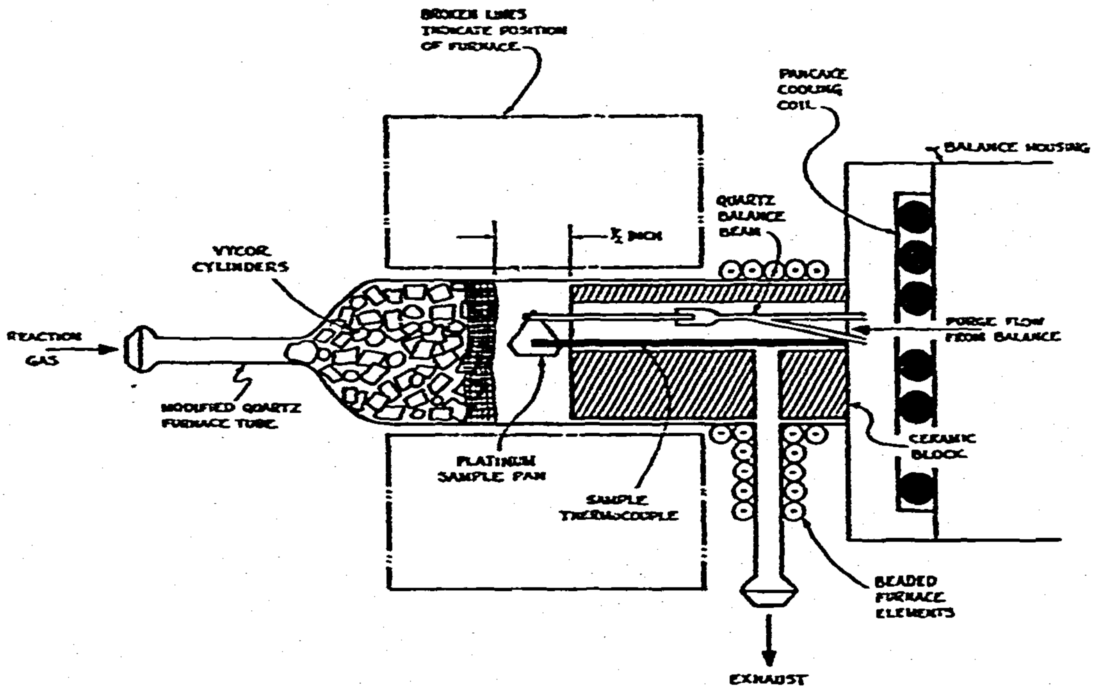


Fig. 3. DuPont TG as modified for the study of high pressure–temperature sulfur acceptor chemistries.

Eventually, the configuration shown in Fig. 3 was adopted. The open space containing the sample pan was reduced to 0.5 in. by completely filling the downstream section of the furnace tube with a ceramic block attached to the balance housing. With refractory surfaces closely surrounding the sample from all directions and with uniform gas and surface temperatures, both the sample and sample thermocouple are now able to "see" the same temperature. This was confirmed by uniform readings of furnace wall and sample thermocouple temperatures and by satisfactory calibration of the melting point standards at all pressures.

A routine procedure, based on the more accurate Perkin–Elmer magnetic standards has since been adopted for calibrating temperatures[19]. This procedure is executed every time a different set of gas compositions or pressure is planned.

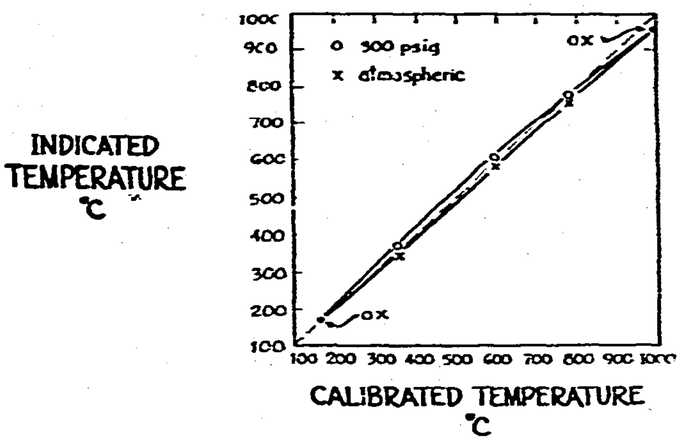


Fig. 4. Temperature calibration of TG using magnetic standards.

Figure 4 shows the results of a series of calibrations made at low and high pressures. A maximum difference between readings at low and high pressures of 25°C occurs at about 500°C. This should be compared with a maximum difference of 100°C obtained without the present modifications to the TG. In general, the indicated temperature was found to be accurate to within 15°C, except for temperatures beyond 800°C where indicated temperatures begin to lag behind "true" temperatures. At 1000°C the indicated temperature for low and high pressure alike lags by 35°C. While the accuracy of the indicated temperature is something to be desired, with calibration the sample temperature can be reproducibly determined to within 5°C.

The present modifications of the TG also solved another serious problem which was encountered with the earlier configuration. When running with steam-containing atmospheres at high pressure, significant condensation took place on the quartz balance beam or in the narrow slot between the beam and the aluminum balance housing. This was not entirely unanticipated since mixing of the cold purge gas with the steam-laden reaction gases must take place in the cooler regions of the furnace tube adjacent to the balance housing. Simply providing external heating to the exposed sections of the furnace tube did not alleviate the problem. Apparently, the formation of convection cells, which had earlier interfered with the measurement of temperature, was also responsible for mist formation and condensation.

The ceramic block design was able to solve the condensation problem by preventing the formation of convection cells. Reaction gases leaving the sample area now mix with the purge gas in a *narrow* passage in the hot ceramic block, which also houses the balance beam. A separate passage in the ceramic block houses the sample thermocouple; this passage is not shown in Fig. 3. The combined gas flow is then vented through the hot ceramic block by a narrow transverse passage which leads to a sidearm in the quartz furnace tube. With this configuration steam partial pressures up to 20 atm have thus far been used without difficulty.

The ceramic block also provides for effective separation of reaction and purge gases. On the basis of penetration tests a reaction gas flow-rate of 100 ml min^{-1} was found sufficient to prevent purge gas penetration into the reaction zone at 300 psig. The penetration tests were carried out using oxygen as the purge gas, nitrogen as the reaction gas, and a finely divided copper powder sample maintained at 600°C as an oxygen detector.

Several failures of the balance movement, at first thought to be the result of intermittent H_2S penetration, were soon more accurately traced to damage caused by overheating from the adjacent beaded heating elements surrounding the furnace tube. An 1/8 in. pancake cooling coil on the face of the aluminum balance housing has been installed and no breakdowns have since been experienced (see Fig. 3).

Flow system for the pressure thermobalance

The principle difficulty in designing a high pressure dynamic flow system for the thermobalance with corrosive gas atmospheres is the absolute necessity for maintaining stable flow of gases while providing continuous balancing of pressure inside the thermobalance with its surrounding atmosphere. Unsteady flows to the pressure thermobalance can result in the inadvertent introduction of corrosive gases into the balance housing.

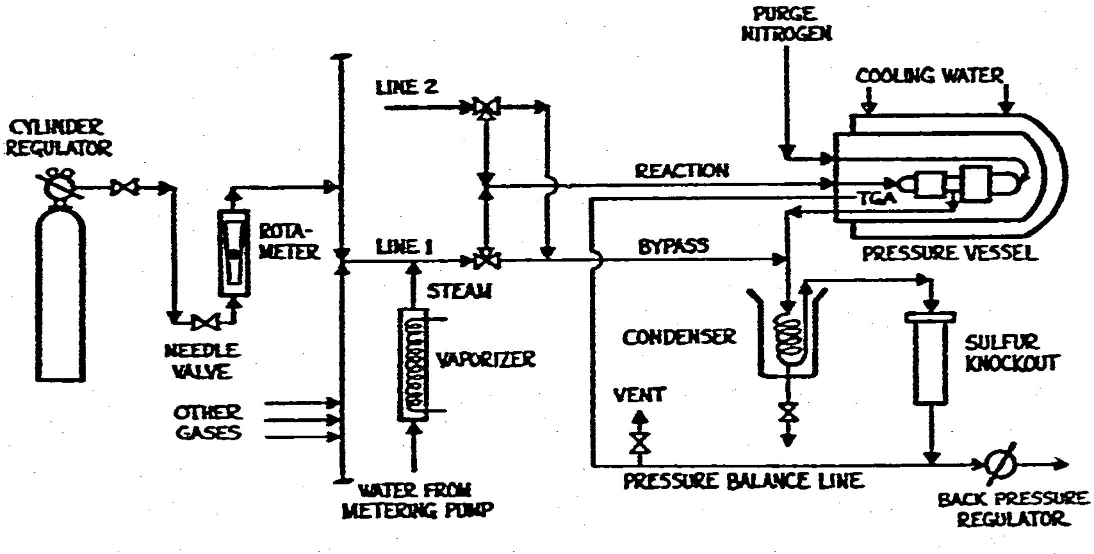


Fig. 5. Schematic of complete set-up for high pressure thermobalance.

Figure 5 is a schematic of the flow system for the pressurized thermobalance. Inlet pressures of the various gases are controlled using standard cylinder regulators. Lo-flow regulated rotameters are used for flow measurement and control of the individual gases. System pressure is maintained by a lo-flow back pressure regulator (hand-loading, piston type) through which all gases are vented.

In order to prevent damage to the back pressure regulator the gases are first dried in a condenser at 0°C and then desulfurized in a zinc oxide bed. These precautions were reported[13] to be necessary in order to prevent sulfur deposition in the back pressure regulator when operating with H_2S-laden gases.

Balancing of pressures inside the TG with its surrounding atmosphere is achieved by providing continuity of the bomb atmosphere with the exhaust gas line following the zinc oxide bed.

A separate gas line carries purge nitrogen directly to the rear of the thermobalance, thus insuring positive flow of purge gases at all times. During pressurization, however, purge nitrogen is first directed to the pressure vessel itself. This permits rapid pressurization to take place without adversely affecting the balance. This reservoir of nitrogen remains in the vessel throughout a run until depressurization. Rapid depressurization is achieved by throttling from the pressure balancing line directly (see Fig. 5).

The reaction gas flow system is designed with duplicate sets of feed lines. This permits one reaction gas mixture to flow into the thermobalance while another gas mixture is either being prepared or awaiting the next phase of a reaction cycle. A system of three-way solonoid valves, situated close to the pressure vessel, instantaneously switches one reaction gas stream to the thermobalance while diverting the other reaction gas stream to the condenser for venting, thus bypassing the thermobalance. This design also anticipates future needs for studying short residence time kinetics.

Steam generation for the high pressure TG

Three basic methods were considered for generating controlled amounts of steam: hydrogen-oxygen burner; gas saturator; and vaporizer using metered flow of liquid water.

The first scheme has been used successfully by Pell[20] and Ruth[18] in their researches at atmospheric pressure. It avoids the difficulties associated with vaporizing liquids and is easily calibrated. However, at high pressures this technique was considered risky due to expected high heat release concentrations and the fine degree of control needed for its operation.

Saturation always involves a certain degree of uncertainty, especially for small gas flows.

The last technique was finally adopted for its simplicity and safety. A high pressure LC single stroke pump was used to meter liquid water to a small packed bed vaporizer. The accuracy of the flow-rate of steam with this technique is better than 3%. In all runs, approximately 95% of the steam fed was directly recovered in the condenser.

Difficulties with feeding high concentrations of steam at pressure were experienced with the above system. Condensation occurred inside the balance housing; no amount of purge flow or auxiliary heating of the ceramic block was able to prevent its occurrence. The source of the problem was identified to be the very nature of the vaporization process itself. Vaporization is not a steady-state process, but takes place explosively as each droplet is converted to vapor. The dynamics of the flow system for the high pressure thermobalance are such that any pulses generated during vaporization could be propagated as far as the balance housing. Dynamic analysis of the system confirmed that unsteady-state penetration of steam into the balance was indeed possible and also indicated the solution. Pulseless flow of steam was finally achieved by placing a surge volume and an orifice in the steam line to the thermobalance.

Continuous weight measurement with the high pressure TG

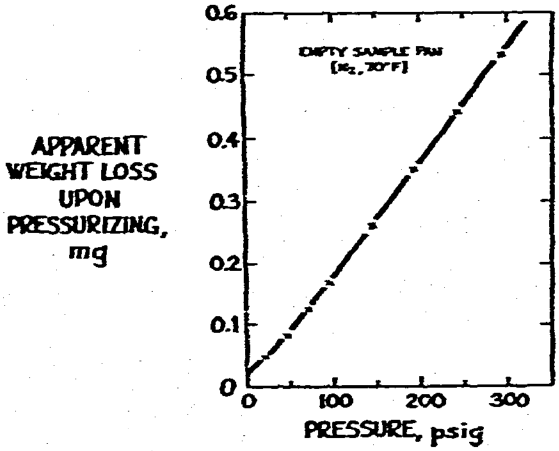
The design modifications incorporated into the DuPont TG did change some of its operating characteristics. For example, at atmospheric pressure the baseline weight was found to continuously increase with temperature (~0.07 mg per 100°C) and total gas flow-rate (~0.08 mg per 100 ml at 25°C and ~0.19 mg per 100 ml at 925°C). These effects, normally not observed with the original DuPont instrument, are attributable to aerodynamic drag forces exerted by gases flowing over the quartz balance beam as they exit out of the ceramic block (see Fig. 3).

On the other hand, weight changes observed in going to pressure are entirely attributable to buoyancy effects caused by basic design features of the DuPont balance. In particular, the small difference in volumes of the balance arms in the DuPont TG will result in a linear decrease in baseline weight with increasing pressure, as shown in Fig. 6. This linear dependency is also predicted by the relation[11]:

$$\Delta R_p = (V_l - V_r)\Delta\rho_g \propto (V_l - V_r)\Delta P \qquad (1)$$

where ΔR_p = shift in baseline weight with increasing pressure
$\Delta\rho_g$ = change in gas density due to increasing pressure ΔP
V_r, V_l = effective volume of right and left balance arms, respectively.

A value for $(V_l - V_r)$ of 0.023 ml can be calculated from the slope of the plot in Fig. 6.



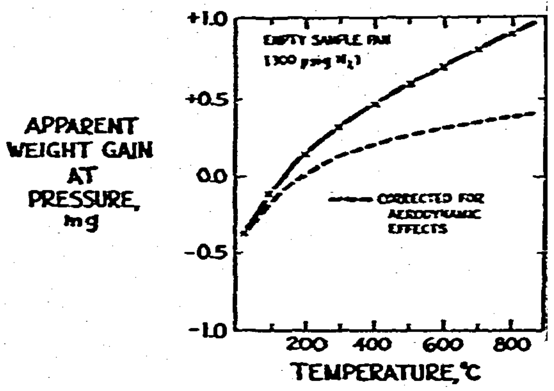


Fig. 6. Effect of increasing pressure on baseline weight.

Fig. 7. Effect of increasing temperature at 300 psig on baseline weight.

Figure 7 shows an increase in baseline weight obtained at 300 psig with inincreasing temperature. The sharp initial rise is attributed to the reduction in gas density in the hot reaction zone, while the slower linear rise at the higher temperatures simply reflects the aerodynamic effects discussed earlier. Employing the same principles used in developing eqn (1), we obtain the relation[11]:

$$\Delta R_t = V_h \Delta \rho_g \propto V_h \left[\frac{1}{T_c} - \frac{1}{T_h} \right] \tag{2}$$

where ΔR_t = shift in baseline weight at pressure with increasing temperature
V_h = effective volume of left balance arm in hot zone
$\Delta \rho_g$ = change in gas density in hot zone due to increasing temperature
T_c, T_h = ambient and hot zone temperatures, respectively.

The above equation predicts a linear relationship for the shift in baseline weight with the inverse absolute temperature in the hot zone; i.e., the sample temperature. After correction for aerodynamic effects (0.07 mg per 100°C), Fig. 7 was accordingly replotted in Fig. 8, from which a value of V_h of 0.0412 ml was calculated from the slope.

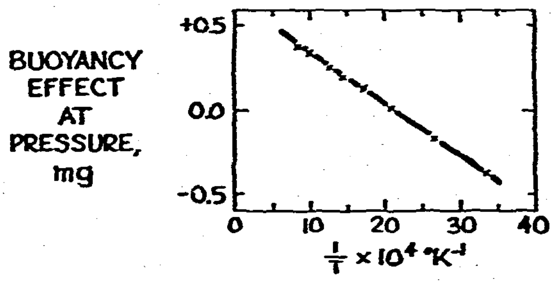


Fig. 8. Buoyancy correlation for effect of increasing temperature at 300 psig on baseline weight.

The above discussions serve to illustrate that not only are these shifts in baseline weights explainable but they are also easily amenable to calibration. These calibrations, have, in fact, been used by many investigators to correct TG temperature scans in order to extract the "true" scans[8,11]. There is even one report of a high pressure instrument with built-in circuits for automatic compensation of buoyancy effects[7].

When operating in the isothermal mode, the above calibration procedure becomes unnecessary since all calculations will then be made relative to the apparent starting weight just prior to the run. However, a buoyancy correction to the apparent weight change for a sample undergoing reaction is still required in order to relate it to a "true" weight change. This correction factor is given by the relation:

$$\Delta w = \left[\frac{\rho_g}{\rho_p} + 1 \right] \Delta w' \tag{3}$$

where $\Delta w'$, Δw = apparent and real weight change at isothermal conditions
ρ_g = gas density
ρ_p = mean particle density of starting and final solid.

In most cases the above correction is usually very small and can be neglected. For half-calcined dolomite at 300 psig and 800°C this correction corresponds to only 0.3% of the sample weight.

APPLICATIONS TO PROCESS STUDIES

A preliminary series of experiments with the high pressure TG was carried out looking at the cyclic CO_2-acceptor reactions for half-calcined dolomite $[CaCO_3+MgO]$.

$$[CaCO_3+MgO] \rightarrow [CaO+MgO]+CO_2 \qquad (I)$$

$$[CaO+MgO]+CO_2 \rightarrow [CaCO_3+MgO] \qquad (II)$$

These reactions form the basis for Consol Coal's CO_2-Acceptor Process for gasifying lignite[21] and play a very important role in the Gesellschaft für Kohlentechnik CO-shift process[22].

Except for information provided by Consol Coal[21,23] and the Gesellschaft für Kohlentechnik[22], there is very little information in the open literature on the cyclability of this material under various calcining and regeneration conditions. A preliminary study was, therefore, undertaken to investigate the effects of various process parameters on the cyclability of calcined dolomite. In particular, the parameters surveyed include: calcination and regeneration temperatures, total pressure, and the partial pressures of carbon dioxide and steam during calcination and regeneration.

In all the cycling experiments, calcination was carried out non-isothermally (20°C min^{-1}) to the calcination temperature corresponding to the CO_2 partial pressure selected. This was then followed by an additional 10 min holding period in nitrogen at the maximum temperature to affect complete calcination. The solid was then cooled in nitrogen to the selected regeneration temperature. Regeneration was carried out isothermally until the reaction ceased to show further activity.

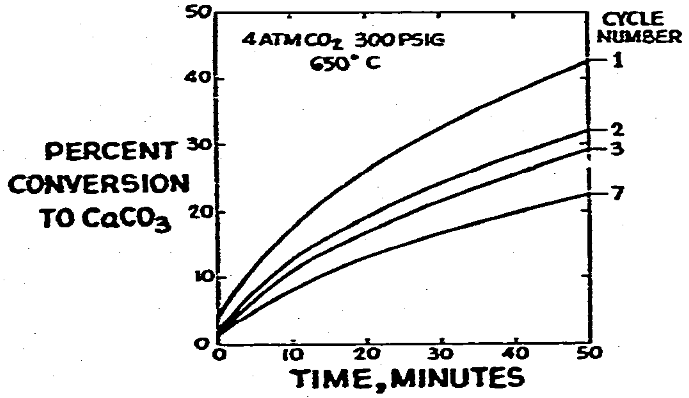


Fig. 9. Cyclic recarbonation of fully-calcined Greenfield dolomite at 650 °C and 300 psig in 4 atm CO_2.

Figure 9 shows the results for calcination/regeneration cycles carried out at 300 psig with 4 atm of carbon dioxide. The temperature for regeneration was 650°C, and the maximum temperature reached during calcination was 1030°C. The observed decline in reactivity with cycling confirms the findings obtained by Consol Coal in their bench scale studies[21,23].

After completion of the preliminary CO_2-acceptor studies, we took to task the investigation of sulfur acceptor chemistries. The process concept of the cyclic use of calcined dolomite for desulfurizing fuels undergoing gasification was first proposed[24] in 1966. Half-calcined dolomite absorbs hydrogen sulfide by the reaction:

$$[CaCO_3 + MgO] + H_2S = [CaS + MgO] + H_2O + CO_2 \qquad \text{(IV)}$$

Regeneration of the solid adsorbent is by the reverse reaction, preferably conducted at the lowest temperature and highest pressure possible in order to obtain the highest possible concentration of hydrogen sulfide in the offgas, facilitating conversion of this species to elemental sulfur in a subsequent operation.

Preliminary bench scale studies indeed confirmed the feasibility of the above process[24]. Subsequently, kinetic studies were carried out in our laboratories at atmospheric pressure using an Ainsworth thermobalance[20,25,26] and a DuPont TG as modified by Ruth[17,18]. These investigations outlined the kinetics for the reaction of both fully calcined and half-calcined dolomite with H_2S. In addition, sulfur absorption and regeneration cycles were made at atmospheric pressure and 750°C. Although the absorption was rapid, the regeneration reaction was slow, requiring more than 1 h. There was a decline in capacity of the solid to about 23% of the total calcium after about 6 cycles.

In going to higher pressures both the kinetics and thermodynamics become much more favorable so that some improvement in the performance of these reactions is anticipated. Figure 10 gives results from 30 cycles at 750°C and 300 psig obtained in our high pressure TG. The capacity at high pressure settled out at about 45%, in

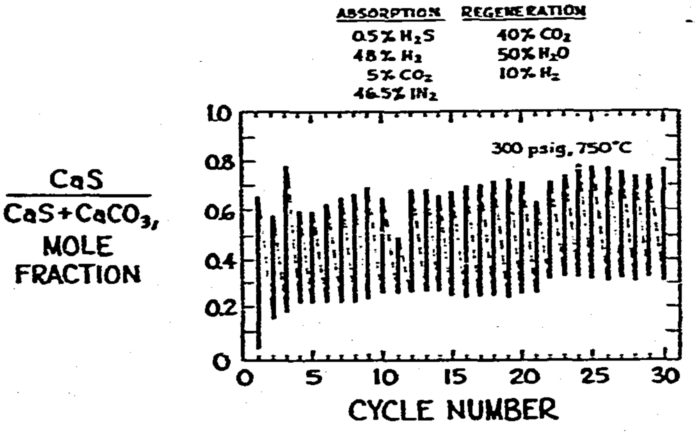


Fig. 10. Cyclic-sulfidation of half-calcined Greenfield dolomite at 750°C and 300 psig.

contrast to the 23% obtained at atmospheric pressure after 6 cycles. The regeneration eaction at 300 psig is extremely fast, running its course in only about 1 min.

Several exploratory runs were also made to determine the effect of desulfurization and regeneration temperatures and the effect of H_2O/CO_2 ratio in the regeneration gas on the cyclability of half-calcined dolomite. It may be noted that we have succeeded in a run of 15 cycles with a steam partial pressure in the vicinity of 18 atm. We are not aware of any DuPont set-up capable of such high partial pressures of steam.

Other research groups including Consol Coal[27], Air Products, U.S. Steel, Westinghouse[12,13] and Huerty of France have followed our lead and have studied the cyclic use of half-calcined dolomite for removing hydrogen sulfide from fuel gases. The Westinghouse effort employs a DuPont TG modified along similar lines to ours. They have thus far reported results for cycling at 10 atm and up to 20% H_2O in the regeneration gas.

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