Calcimeter Instruction Manual

The Hohner Calcimeter is based on industry standard versions, and is used to measure the calcium carbonate and magnesium carbonate in samples.

Introduction (Section 1):

The calcium carbonate and magnesium carbonate are reacted with 10 percent Hydrochloric Acid to form CO_2. This is done in a sealed reaction cell and the pressure build up due to the CO_2 is measured using either a pressure gauge or a pressure recorder. The use of a Calibration Curve, Fig. 4, determined through the use of pure Calcium Carbonate reagent allows the pressure developed to be related to the weight of calcium carbonate in the calibration sample. Several weights of sample are suggested to assure an accurate curve. These tests can be conducted using either the pressure gauge or recorder with the reaction cell. The sample can be weighed on a portable balance (10 mg Precision or better). Refer to Section 5 for calibration procedure.

The calcium carbonate content of the sample is determined by treating a 1 gm dried sample with hydrochloric acid (HCl) in an enclosed reactor vessel. Carbon dioxide gas is evolved during the reaction between the acid and carbonate fraction of the specimen. The resulting pressure generated in the closed reactor is directly proportional to the carbonate content of the specimen. This pressure is measured with a bourdon tube pressure gauge that can be pre-calibrated with reagent grade calcium carbonate. Refer to Section 5 for calibration procedure.

Safety Considerations (Section 2):

The Calcimeter Test depends on reacting $CaCO_3$ with HCl. Hydrochloric Acid may be Corrosive and may cause Chemical Burns. Use care in handling the Hydrochloric Acid so that no acid is spilled on either skin or clothing or splashed into eyes. If acid contacts skin or eyes, immediately flush with large quantities of water for at least 15 minutes. Do not inhale vapours. Process Hydrochloric Acid beneath a laboratory hood or in a well ventilated area to reduce the inhalation of fumes. Wear appropriate safety equipment.

Do not take internally. Get medical attention immediately if accidentally contacted by the acid. Always open the pressure bleed valve of the reaction cell following each test. Do not attempt to open the cell until all pressure has been dissipated. The Calcimeter uses an electrically powered sensor to measure the pressure in the Reaction Cell. The following Safety Considerations should be used with this Recorder as with any electrical appliance:

1. Make sure the Power switch is OFF before connecting power cable to electrical outlet.
2. Verify the power cable and the outlet receptacle are three wire grounding type plug and receptacle.
3. Always unplug the power cable before opening the Recorder for renewing the chart paper or other maintenance or repair work.

Test Procedure (Section 3):

Before testing, make sure the equipment is clean. Verify that a calibration curve is available for the particular equipment to be used. Should a calibration curve not be available, follow the procedures outlined in Section 5 to construct one. For an illustration of this curve Refer to Fig. 4.

A. Obtain a sample of Core, Drilled Cuttings, or other solids that are to be analyzed. The sample should be dry and free of contaminants. Grind sample to 100 mesh or finer, using a mortar and pestle and a 100 mesh sieve. If it is unknown whether the sample has been dried, it is recommended to heat the sample in an oven at 220°F (105°C) for 12 to 24 hours.

B. Weigh approximately (1.0 to 1.4 gms) of the ground sample and record the weight to nearest .001 gm (10 mg)

CAUTION - Do not attempt to run larger than 0.7 gm sample with the 10 ml acid cup.

C. Load the Test Sample in the CO_2 reaction cell.

1. Unscrew and remove the top with pressure gauge or pressure transducer from the Reaction Cell then remove the acid cup.

2. Inspect to be sure CO_2 reaction cell and top are clean and dry.

3. Be sure reaction cell "O" Ring seal on the top, and the "O" Ring on the bleed valve are in good condition. Use a light coating of Vacuum Grease on "O" Ring seals. Make sure all pipe or tubing connections are tight and do not leak. Refer to Section 6A.

4. Slide one paper and its sample to the bottom of the reaction cell by holding cell in horizontal position. Raise cell to vertical and dump sample onto cell bottom. Brush paper with small brush to remove traces of sample then remove the paper.

5. Pour 10 ml or 20 ml of 10% [1 Normal] Hydrochloric Acid (HCL) into the acid cup and cautiously lower the cup into the cell. Be careful not to spill or get any HCL on bottom of cup.

6. Hand tighten cell cap being careful not to splash acid onto sample.

7. Open bleed valve until a Zero pressure reading is obtained on the pressure gauge or on the recorder chart, then close the bleed valve tightly.

    A. Tip the reaction cell and start timing the test. This will start the reaction between the HCl and the $CaCO_3$. Observe the rapidly rising pressure and record it at 30 seconds after the reaction cell was tipped. Record this as $CaCO_3$ pressure. There should be a pause, and then a slow second rise in pressure will be noted if dolomite is present. The dolomite reaction and pressure rise is much slower for dolomite. Swirl reaction cell and allow sufficient time for completion of the pressure build up. The reaction is assumed complete when the pressure stops increasing and remains constant. This should happen in 30 to 45 minutes. This final value of pressure is the total $CaCO_3$ plus dolomite pressure. To obtain the pressure due to the dolomite, subtract the calcium carbonate pressure (30 second reading) from the total reading (30-45 minute reading).

D. For interpretation of the pressure readings. Refer to Fig. 1, 2, and 3. These are representative of pressure versus time graphs as they would appear on a Pressure Recorder Chart. Fig. 1 is representative of the CaCO3 only. Fig. 2 is representative of dolomite only. Fig. 3 is representative of combined CaCO3 and dolomite.

E. Use equations [1] and [2] below for calculation of the percentages of CaCO3 and dolomite. For values of "Slope" refer to Section 5.

[1] $\%CaCO_3$, as recorded

$$= \frac{(\text{Pressure Reading, PSI})\,(100)}{(\text{Sample Weight})\,(\text{Average Slope})}$$

[2] % Dolomite, as recorded

$$= \frac{(\text{Total Press.} - \text{Press. } CaCO_3)\,(100)\,(.92)}{(\text{Sample Weight})\,(\text{Average Slope})}$$

<u>ASTM Standard Test Method for Calcium Carbonate Content of Soils (Section 4):</u>

Before testing, make sure the equipment is clean. Refer to Section 5 to verify that a calibration curve is available for the equipment to be used, and that the equipment uses a 20 ml acid cup. Should a calibration curve not be available, follow the procedures outlined in Section 5 to construct one using the 7 point plot. This ASTM test specifies the use of a 1.00 gm test specimen. For an illustration of the 7 point plot Refer to Fig. 4.

A. Select a 20 to 30 gm. sample of Core, surface grab sample, or other specimen that is to be analyzed. The sample should be dried in an oven at 220 F (105 C) for 12 to 24 hours. Pulverize the sample with a mortar and pestle (or hammer) until all particles pass through a No.10 (2mm) sieve or finer. The finer the sample, the faster the reaction.

B. Weigh out onto as small piece of glazed paper accurately a 1 gm. +/- 10 mg. sample of the specimen as prepared in Section A above.

> NOTE: If pressure response is very low, as will be found in specimens of low calcium carbonate containment, the weight of the sample can be doubled, then dividing the pressure reading by 2 to obtain the correct calcium carbonate content.

C. Load the Test Sample in the CO2 reactor cell.

1. Unscrew and remove the top with pressure gauge or pressure transducer from the Reactor Cell then remove the acid cup.

2. Inspect to be sure CO2 reactor cell and top are clean and dry.

3. Be sure cell "O" Ring seal on the top, and the "O" Ring on the bleed valve are in good condition. Use a light coating of Vacuum Grease on "O" Ring seals. Make sure all pipe or tubing connections are tight and do not leak.

4. Slide one paper and its 1.00 gm. test sample to the bottom of the cell while holding cell in horizontal position. Raise cell to vertical and dump sample onto cell bottom. Brush the paper with small brush to remove traces of sample then remove the paper.

5. Pour 20 ml of 10 percent HCL into acid cup (20 ml is the line on the side of the cup), and lower acid cup into cell. Be careful not to spill or get any HCL on bottom of cup.

6. Hand tighten cell cap being careful not to splash acid onto sample.

7. Open bleed valve until a Zero pressure reading is obtained on the pressure gauge or on the recorder chart, then close the bleed valve tightly.

D. Tip the reaction cell and start timing the test. This will start the reaction between the HCl and the CaCO3. Observe the rapidly rising pressure and record it at 30 seconds after the reaction cell was tipped. Record this as CaCO3 pressure. There should be a pause, and then a slow second rise in pressure will be noted if dolomite is present. The dolomite reaction and pressure rise is much slower for dolomite. Swirl reaction cell and allow sufficient time for completion of the pressure build up. The reaction is assumed complete when the pressure stops increasing and remains constant. This should happen in 30 to 45 minutes. This final value of pressure is the total CaCO3 plus dolomite pressure. To obtain the pressure due to the dolomite, subtract the calcium carbonate pressure (30 second reading) from the total reading (30-45 minute reading).

E. For interpretation of the pressure readings. Refer to Fig. 1, 2, and 3. These are representative of pressure versus time graphs as they would appear on a Pressure Recorder Chart. Fig. 1 is representative of the CaCO3 only. Fig. 2 is representative of dolomite only. Fig. 3 is representative of combined CaCO3 and dolomite.

F. Equations [1] and [2] can be used for calculation of the percentages of CaCO3 and dolomite, however since the sample size is specified as 1.00 gm these equations can be further simplified to equations [3] and [4] respectively.

Since sample weight = 1.00 gm

$$\%CaCO_3 = \frac{Pressure\ PSI\ x\ 100}{Slope} \quad [3]$$

Since sample weight = 1.00 gm,

$$\%Dolomite = \frac{Pressure\ PSI\ x\ 92}{Slope} \quad [4]$$

Figures 1, 2, 3 and 4:

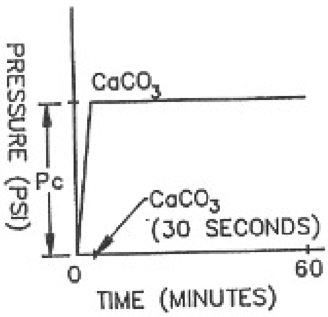

Fig. 1

$CaCO_3$ Pressure

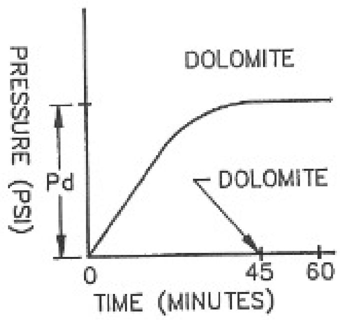

Fig. 2

Dolomite Pressure

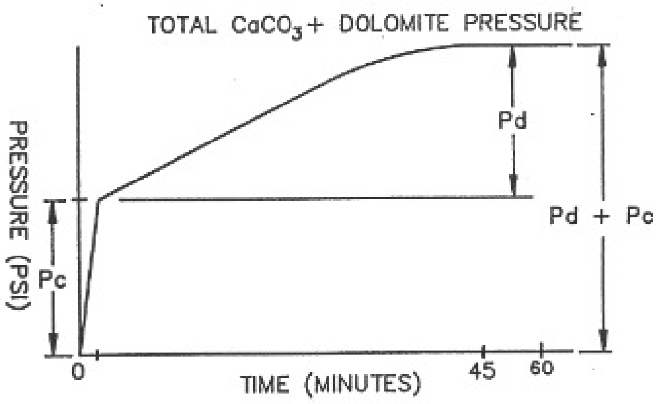

Fig. 3

Total Pressure - $CaCO_3$ + Dolomite

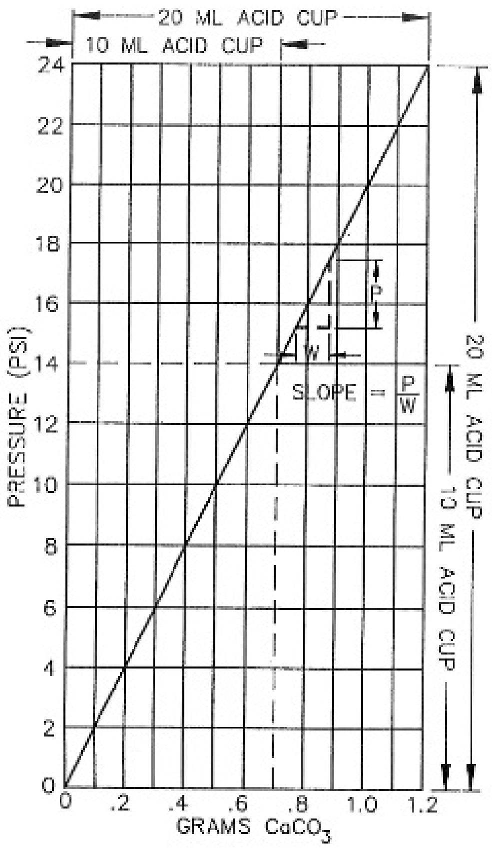

Fig. 4

$CaCO_3$ Calibration Curve

[10 & 20 ml Acid Cups]

Construction of Calibration Curve (Section 5):

The volume of the reaction cell of a Calcimeter of the type used for the Hohner Calcimeter and described in the relationship of the pressure observed to the amount of CO2 released by a given weight of CaCO3 when reacted with HCl. This relationship is a constant for a given reaction cell. The calibration curve or calculated calibration factor (the reciprocal of the slope x 100 percent of the calibration curve x 100 percent) are used to translate the observed pressure resulting from the CO2 released by a given weight of reagent grade CaCO3 to percent calcium carbonate. All points on the calibration curve represent 100 percent CaCO3 for that sample weight. Any number of samples can be used to construct the calibration curve. The following are recommended to give good accuracy.

A. Weigh Out Calibration Samples

1. For 15 psig full scale gauge, 15 psig full scale recorder and a 10 ml acid cup, weigh exactly .200, .400, .600, and .700 gms of Reagent Grade CaCO3 onto small pieces of glazed paper for calibration.

2. For 30 psig full scale gauge, 30 psig full scale recorder and a 20 ml acid cup. weigh out additional samples of .800, 1.000 , and 1.200 gms CaCO3.

NOTE: Do not use samples of CaCO3 larger than .700 gms unless a 20 ml acid cup is available.

B. Load a Calibration Sample.

Perform the procedure outlined in Section 3-C for Hohner Test Procedure, Steps C-1 through C-7.

C. Tip the cell and allow acid to run out of cup onto the sample. Swirl gently and continuously until a constant pressure is obtained. This will usually take about 30 seconds. Keep reactants in lower part of cell to avoid getting acid into pressure gauge or pressure transducer. As soon as the reaction is started observe the rapidly rising pressure. Record this pressure at its peak. Record this as the CaCO3 pressure for the sample weight used.

NOTE: If a mechanical shaker is available, it may be used to agitate the cell rather than swirling the reactants as described above. Agitate the sample for 10 minutes.

D. Repeat the procedure outlined in Section B and C above for each of the samples prepared in Section A above. This will be a total of four samples if a 15 psig gauge or Recorder and a 10 ml acid sample cup are being used or a total of seven samples if a 30 psig gauge or recorder and a 20 ml acid cup are being used.

E. Plot grams of CaCO3for each sample verses final pressure reading for each sample on linear graph paper. Draw a straight line averaged through these points. A sample graph for the four point plot and the addition for the 7 point graph is shown in Fig. 4. Larger samples of CaCO3 cannot be reacted using the 10 ml acid cup.

F. Note the linear relation between the pressure and sample size, therefore this curve may be assumed to be a straight line, and its slope will be a constant. As illustrated in Fig. 4 the slope of the curve is 2 psig /.1 gm CaCO3, or 20 psig / 1.0 gm sample, resulting in a slope of 20. Therefore the Calibration Factor in this case is 1/20 = .05 x 100 or 5. This number is the slope or average slope for the particular equipment calibrated. It is a function of the volume of the reaction cell. As shown by equations [5] and [6] below the slope can be written as a "Cell Factor" to multiply the pressure reading by to directly obtain percentages of Calcium Carbonate and Dolomite.

As described above Slope = 20 psig for a 1 gm sample therefore

[5] $$\%CaCO_3 = \frac{Pressure\ x\ 100}{1\ gm\ x\ 20}$$

or

$$\%CaCO_3 = 5\ x\ Pressure$$

[6] $$\%Dolomite = \frac{(Total\ Press\ -\ CaCO_3\ Press)(.92)(100)}{1gm\ x\ 120}$$

or

$$\%Dolomite = 4.6\ x\ (Total\ Press\ -\ CaCO_3\ Press)$$

Maintenance and Repair (Section 6):

A. Testing For Leaks

Leaks in the pressure system are probably the greatest source of potential trouble.

1. Periodically inspect Reaction Cell and replace O-Rings if necessary.

2. Check the pipe thread connection between the reaction cell top and the pressure Gauge or transducer with a brush and soap suds. Repair by disassembling the pipe threaded connection between the reaction cell and the gauge or transducer. Use Locktite pipe sealant with teflon or similar product.

3. Check for plugging in the connection between reaction cell and gauge or transducer, also in the gauge entrance or the transducer barrel and diaphragm for build-up of calcium deposit over long periods of time. A warm Chlorox wash should clean these parts.

4. To check for leaks, pressurize the instrument as described in Section 5 -A1 and B. using a .6gm. sample and let stand at least one hour. Pressure should not decrease unless leaks are present.

B. Calibration Data Does Not Give a Straight Line If there are no leaks in the system, but results are not giving a straight line calibration curve or data is otherwise questionable check the following:

1. Check for sticking pressure gauge or recorder malfunction.

2. Make sure the scale or balance is clean and free of corrosion on weights and pans. Shield balance from air currents and vibration as much as possible when weighing sample or $CaCO_3$ for calibration.

3. Check Reaction Cell for contaminants. Be sure cell is clean and dry.

4. Check for impurities in reagents. Moisture in $CaCO_3$ standard will result in low pressure readings.

Parts List (Section 7):

Pressure Sensor:	ProSense EPS25-36-1001
Cable and Connector:	CD12L-0B-020-A0
Pressure Relief Valve:	Swagelok SS-4P-2M
O-Ring:	Hohner CAL-O-Ring-1
Cap:	Calcimeter-Cap
Sample cup with stick:	Calcimeter-Spoon
Bottle:	Calcimeter-Bottle

Calcimeter Assembly Instructions

Parts List

Pressure Sensor:	ProSense EPS25-36 1001
Cable and Connector:	CD12L-0B-020-A0
Pressure Relief Valve:	Swagelok SS-4P-2M
O-Ring:	Hohner INHO
Cap:	Calcimeter-Cap
Sample cup with stick:	Calcimeter-Spoon
Bottle:	Calcimeter-Bottle

Step 1) Before assembly refer to user manual and maintenance sections here: http://hohneroilgas.com/OilField/Calcimeter_Manual.pdf

Step 2) The Pressure Sensor should be screwed into the Cap and torqued to 10Nm.

Step 3) The Pressure Relief Valve should be screwed into the Cap and hand tight with a final twist using a spanner

Step 4) A sample can now be added to the Cup and Stick.

Step 5) Place the Cup and Stick inside the bottle.

Step 6) Ensure that the O-Ring is fitted in the bottle groove and tighten down the lid until it is hand tight.