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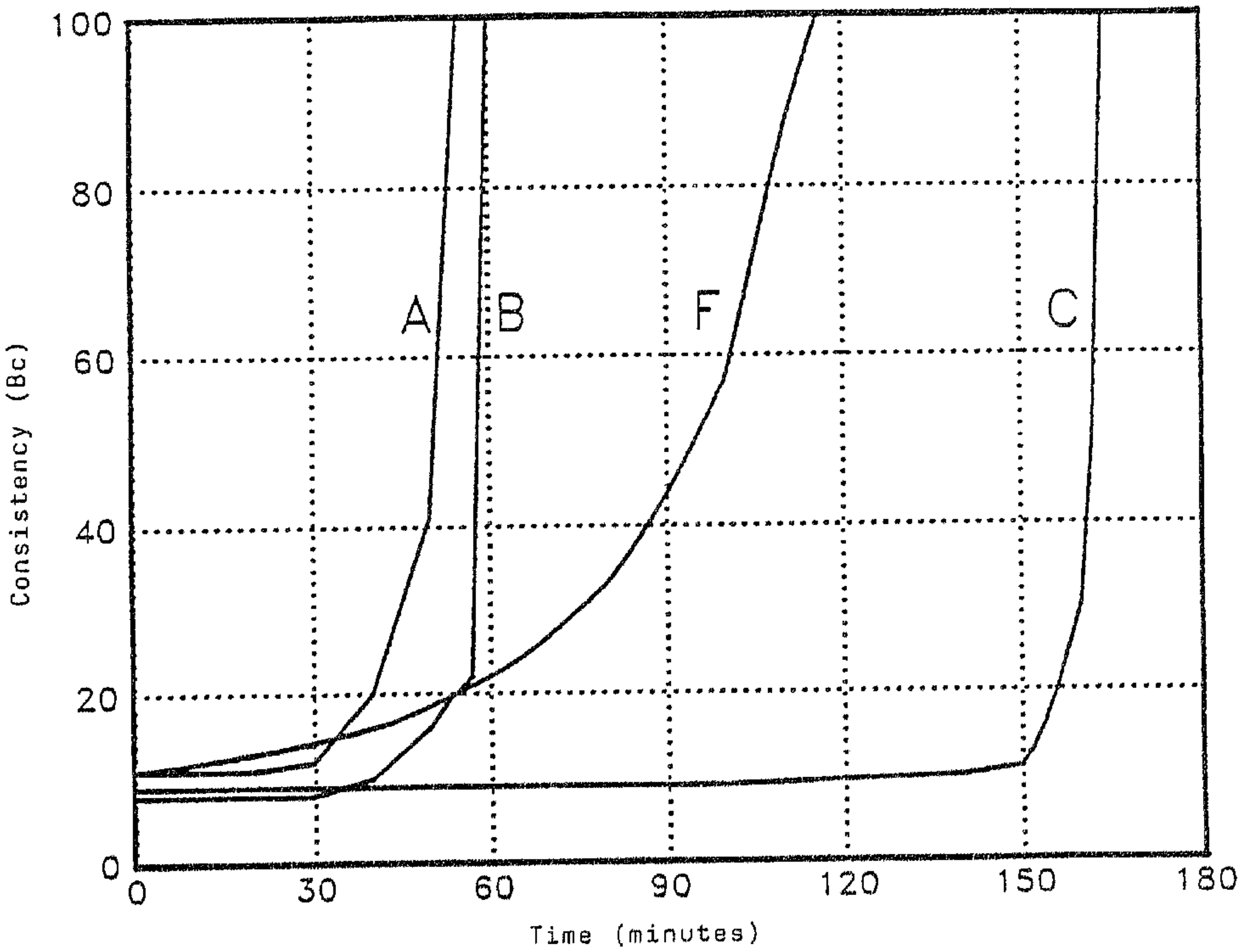
(54) Title: COMPOSITION FOR CEMENTING OIL WELLS AT LOW TEMPERATURE



(57) **Abrégé/Abstract**:
A slurry composition for cementing oil, gas, water, geothermal and analogous wells comprises plaster, cement and microsilica. The slurry has applications to gas migration control at low temperatures and under conditions necessitating fast setting of the cement slurry.

ABSTRACT

A slurry composition for cementing oil, gas, water, geothermal and analogous wells comprises plaster, cement and microsilica. The slurry has applications to gas migration control at low temperatures and under conditions necessitating fast setting of the cement slurry.

COMPOSITION FOR CEMENTING OIL WELLS AT LOW TEMPERATURE

The present invention applies to the field of oil and associated industry services, and, in particular, that of cementing the annulus of an oil, gas, water, geothermal or analogous well.

Such cementing operations, as well as their importance for the life and production of the well, have been known to the man of the art for several decades and there is no need to reiterate the principle and details thereof.

It will simply be mentioned, to permit correct understanding of the text and of the invention, that it involves injecting a cement slurry into the casing of the well. This cement slurry goes downhole through the casing and then, under the pumping pressure, returns upwards through the annulus between the borehole and the casing, up to the surface of the well. There exist perfectly conventional methods for ensuring that, upon completion of pumping, the inside of the casing contains an inert fluid, and not the slurry. The cement slurry is then allowed to set.

The general object of the operation is to maintain the casing in the well, to isolate the underground areas traversed and to consolidate the well itself.

The cement slurry is pumped under pressure, and passes from the on-surface preparation conditions (ambient pressure and temperature) to the downhole conditions (higher pressure and temperature), part of the slurry then returning through the annulus to conditions close to those of the surface. Under certain conditions, in arctic areas or in submarine wells in the North Sea, for example, the surface conditions can be very cold and ensuring that the slurry sets correctly poses quite special problems.

Despite such pressure and temperature cycles, the slurry must, of course, remain pumpable; it must perfectly displace the drilling mud (a critical factor in ensuring that the cementing operation is carried out correctly), it must not sustain any fluid loss in the areas it passes through, and it must set as swiftly as possible, but precisely at the point intended, i.e. up the height of the annulus, and under no circumstances, of course, inside the casing. Finally, the hardened cement must possess excellent mechanical properties and, in particular, good compressive strength, which must develop as quickly as possible after setting.

When the well passes through a gas-containing area, it is extremely important for the hydrostatic pressure exerted by the column of fluid in the annulus to remain greater than the gas pressure in the formation throughout the cementing operation. The density of the drilling fluids, as well as that of the cement, are thus adjusted accordingly.

Once the slurry is in place, it will begin to set. This setting is firstly reflected by the gelation of the slurry. Bonds are created between the cement particles, as well as between the cement and the walls of the well. Owing to these bonds, the column of cement supports itself, which is accompanied by a reduction in the hydrostatic pressure exerted opposite the gas-containing area. During this period, the viscosity of the cement is not yet sufficient to resist the migration of gas bubbles. The end of this period corresponds to hydration, which is an exothermal reaction between the cement and the water reflected by a temperature rise, the development of compressive strength and the chemical shrinkage of the system. During this phase, the pressure opposite the gas-containing area decreases even further and space is created in the form of porosity in the cement matrix, through which the gas can then migrate.

Throughout the setting time, the cement must be capable of withstanding invasion by the gas, which would have serious consequences, ranging from poor cementing to a disastrous gas blowout on the surface.

The mere enumeration of the requisite properties, which are often mutually conflicting or contradictory, the temperature and pressure conditions, and the serious or disastrous consequences arising from failure to observe the properties, gives an indication of the difficulties involved in developing a slurry having the properties in question.

The invention provides a cement slurry that possesses all of the properties enumerated above, and which is thus particularly suitable for the most difficult wells, notably those that pass through gas-containing areas, and having low surface temperature, i.e. the wells that accumulate the greatest difficulties.

According to one aspect of the present invention there is provided a cement slurry composition for oil, gas, water, geothermal and analogous wells, comprising cement, 66 to 150% alpha plaster by weight of cement, 15 to 25% microsilica by weight of cement and plaster, and 30 to 50% water by weight of the cement and plaster. The invention also provides for the use of such a cement composition in cementing oil, gas, water, geothermal and analogous wells. The cement slurry compositions preferably contain, apart from the mixing water:

- alpha plaster,
- ordinary Portland cement (API class A or C),
- microsilica, and, insofar as necessary,
- a retarder and a dispersing agent.

Cementing a well at low temperature (in particular <30°C) presents very special difficulties. In particular, it is difficult, in the case of such wells, to obtain reasonable setting for the cement slurry after several hours and compressive strength in the order of 3500 kPa after eight hours. It should be noted that the setting time is the time required for the consistency of the slurry measured using a consistometer in accordance with API Standard No.10 to reach 100 Bc (Bc: Bearden consistency).

Known accelerating agents, such as calcium chloride, can provide a solution, but with a slow increase in consistency up to 100 Bc and, when setting commences, it takes several hours for the cement to harden. During this lapse of time, unacceptable shrinkage occurs and there is a possibility of gas migration. In addition, below 15oC, it is very difficult to obtain acceleration.

It is already known (USP 3,891,454) to use plaster (semi-hydrate calcium sulphate, $CaSO_41/2H_20$) in a cement slurry to reduce the setting time. This involves replacing the cement by a plaster-cement mixture in a mass ratio ranging from approximately 50:50 to 75:25. However, the addition of plaster to a cement slurry can entail serious drawbacks.

In the first place, the setting time depends very much on the type of plaster. In particular, most plasters are far too reactive in the presence of cement, and we often observe an acceleration of setting at low temperature, which is, in the oil industry, a serious drawback (see above). The over-fast setting can be compensated for, in certain cases, by a large quantity of setting retarder, but then setting can take days.

In the second place, plaster/cement systems have practically zero filtrate control. Finally, plaster is known to be a thixotropic agent in the case of cement, whereas, according to the invention, a fluid slurry is sought after.

Microsilica has already been used in a cement slurry (GB 2,179,933; GB 2,212,150; GB 2,212,489). This is a by-product derived from the manufacture of ferrosilicons. The microsilica particles have a mean size of approximately 0.15 microns and a specific surface in the order of 20 mg^2/g. Owing to the difficulty involved in manipulating fine particles in a raw condition, it is preferred to use microsilica in suspension in water.

However, at low temperature and in the range of concentration in which it has to be used, the microsilica prolongs the cement setting time and delays the development of compressive strength, thereby further impairing one of the essential properties of gas migration control.

Unsurmountable drawbacks were thus encountered in prior art.

The invention provides a system that solves for the first time the cumulative problems posed by cementing at low temperature (approximately 0-30°C) and the need for a system capable of ensuring good gas migration control.

There are known to be two main categories of plaster: alpha and beta type semi-hydrate calcium sulphate, hereinafter referred to as alpha plaster and beta plaster. Their difference originates essentially from the preparation process. Alpha plasters are prepared under controlled steam pressure, whereas beta plasters are produced using a continuous fluidized bed process. Alpha plasters have an apparent density of approximately 1000 kg/m^3, with spherical particles, whereas beta plasters have an apparent density of approximately 600 kg/m^3 and take the form of platelets.

Figure 1 below shows the development of consistency as a function of time for different types of plaster. The operating conditions are as follows: 60 % plaster, 40 % cement, API class A, density 1.89 kg/l, with testing at 20°C.

Curves A, B and C correspond to alpha plasters and offer the highly desirable characteristic of right-angle set. Two beta type plasters, D and E, led to uncontrolled flash setting immediately upon mixing. Curve F corresponds to a beta plaster for which it proved possible to obtain a reasonable setting time through the use of retarder without, however, obtaining either a right-angle set or good compressive strength in the short term.

A right-angle set correspond to a very fast increase in consistency at the time of setting, only a few minutes being taken to increase from 30 Bc to 100 Bc.

It will be remembered that right-angle setting is one of the parameters that plays a part in gas migration control. These results show that the use of alpha plaster in the present invention is of absolutely prime importance.

Figure 2 shows the influence of temperature on setting time, in the case of a system with 60 % alpha plaster, 40 % API class A cement and a density of 1.89 kg/1. Unlike cement, the setting time of which is reduced as the temperature increases, the opposite is observed in the case of a plaster/cement system. The aforegoing shows the complex nature of the physico-chemical mechanisms involved in the invention.

Table 1 hereinafter groups together the results obtained concerning the thickening time (TT) and compressive strength (CS) after 8 or 48 hours. Use was made of an alpha plaster available from Lambert Corporation, an ordinary Portland cement (CPA-HP), slurry density 1.89 kg/1, temperature 20°C, 0.3 % by weight of dispersing agent (sodium/formaldehyde polynaphtalene sulphonate or "PNS") and the retarder is sodium or calcium lignosulphonate.

TABLE 1

Plaster Weight %	Cement Weight %	Retarder Weight %	TT h:min	CS at 8 h kPa	CS at 48 h kPa
60	40	0.6	3:50	8015	13405
50	50	0.6	3:35	7700	15750
40	60	0.7	3:17	6160	13335
30	70	0.8	3:52	1575	12320

The larger the quantity of cement, the shorter the plaster thickening time. However, a retarder such as lignosulphonate makes it easy to adjust the thickening time, under the test conditions according to Table 1 above.

Furthermore, it is very clearly observable that compressive strength after 8 hours is ensured by the setting of the plaster and that the useful range for the alpha plaster in order to obtain compressive strength in the order of 3500 kPa at 8 hours is beyond 30 % by weight of the mixture.

According to the invention, it is essential to incorporate into the plaster/cement system a considerable quantity of microsilica, in particular for applications in which gas migration control is required. The proportion of microsilica will be preferably between 15 and 25 % by weight approximately of the plaster/cement mixture. This quantity is required owing to the need to ensure that the system has a filtrate control value of less than 100 cm^3/30min (see Table 2 hereinafter). The use of microsilica in such proportions has, surprisingly, only a minor effect on the increase in the rheology of the system, which can easily be reduced through the use of a conventional dispersing agent of the "PNS" type. It is further observed that the presence of microsilica makes the slurry particularly stable, which is reflected by the complete absence of free water and sedimentation.

During development of the invention, serious difficulties were experienced in connection with gelation problems when using certain oil well cements of class G in particular. This drawback is removed if use is made exclusively of Portland cement (API Class A or C). Furthermore, preference should be given to ordinary Portland cements.

To obtain sufficient compressive strength within a short space of time (8 hours), and in the presence of high microsilica concentrations, it is essential to use in the system a sufficient quantity of plaster. On the other hand, it can be observed that an excessive quantity is prejudicial to the long-term mechanical properties of the system. Consequently, we shall confine ourselves in the present invention to plaster/cement mixtures having mass ratios ranging from 40:60 to 60:40, a proportion of 60:40 being generally the most suitable (see Table 3 hereinafter).

It is observed that the nature of the alpha plaster, as well as the variety of ordinary Portland cement, only have a slight effect upon the properties of the system (Tables 3 and 4 hereinafter). Similarly, the right-angle setting property sought after is not affected either by the plaster/cement ratio or by the presence of microsilica in the proportions recommended in the invention.

Most of the systems studied during development of the invention have a density of 1.89 kg/l. They contain à 60:40 plaster:cement mixture, to which is added 20 % of microsilica by weight of the mixture. Under these conditions, the quantity of mixing water is 40 % by weight of the plaster/cement mixture. It is possible to lower the density of the slurry without affecting either the stability or the rheology; on the other hand, filtrate control and compressive strength will be considerably reduced. To remain within the framework of the invention, in which the object is to obtain a slurry having good anti-gas migration properties, the lower limit for density is 1.80 kg/l, which corresponds to a quantity of mixing water representing 50 % by weight of the plaster/cement mixture.

From reading the present description, together with Tables 1 to 4 and Figures 1, 2, 3, 4, 5, 6 and 7, a man of the art will appreciate that a representative composition of the invention is characterized in that it contains essentially :

- cement,
- 66 to 150 % of alpha plaster in relation to the weight of the cement,
- 15 to 25 % by weight of microsilica in relation to the weight of the cement + plaster mixture,
- 30 to 50 % of water in relation to the weight of the cement + plaster mixture,
- and possibly a retarder and a dispersing agent.

On the other hand, higher densities can easily be contemplated, but these are often of no practical value in respect of the operations to which the invention especially relates.

The plaster/cement/microsilica systems described above thus possess certain characteristics essential to gas migration control: stability, low rheology, good filtrate control, right-angle set and swift development of compressive strength.

There is no existing API standard test designed to measure the capability of a cement slurry to retain gas. The method used for this invention is briefly described below.

A 33 cm high cell (Figure 3), closed at the upper end, is filled with cement slurry and placed in a thermostatically controlled container. The particular shape of the cell has been developed to avoid experimental artefacts and to force the gas to migrate inside the cement, and not at the cement/wall interface. The bottom of the cell is connected to a nitrogen line at a pressure of 17.5 bar. During the experiment, measurements are made of the pressure at the top of the cell, the temperature of the slurry and the flow rate for nitrogen entering the cell.

Throughout the gelation period, see above, the slurry behaves like a liquid that integrally transmits the gas pressure. During this period, the pressure measured at the top of the cell remains constant, as do the gas flow rate and the temperature. Then comes the exothermal part of hydration. This is reflected by a temperature rise, chemical shrinkage of the cement and development of compressive strength. The pore pressure in the cement matrix drops owing to the space created by chemical shrinkage. According to the system studied, the gas will penetrate the interior of the cement to a varying extent. A system will be termed resistant to gas invasion if the pressure at the top of the cell decreases and if the gas entry rate remains low, or better still, nil.

The physical behaviour of a plaster/cement system is illustrated in Figure 4. It relates to a system containing 60 % by weight of alpha plaster and 40 % of API class A cement (CPA-HP). The first temperature peak, at approximately 3 hours, corresponds to the setting of the plaster and we can observe, at the same time, a gas entry peak to fill the pores created by the chemical shrinkage of the system. At between

8 and 20 hours, approximately, we observe a second gas entry which corresponds to the setting of the cement. Throughout the experiment, the gas pressure is transmitted to the top of the cell, there has been gas migration through the system and permanent communication between the bottom and the top of the cell.

If, in the course of a gas migration experiment, there is permanent communication between the bottom and the top of the cell, the total quantity of gas entering the cell is equal to the quantity of chemical shrinkage. In the course of the experiment illustrated in Figure 4, the total quantity of gas corresponds to 7 % of the volume of the cell, whereas, for a cement alone, we observe only 4 % of shrinkage during this stage. The inner shrinkage of a plaster/cement system is thus very markedly greater than the shrinkage of cement alone which favours gas invasion, which was naturally considered to be a serious drawback by a man of the art.

The effect of the microsilica is indicated in Figure 5, wherein 20 % of microsilica per weight of plaster plus cement have been added to the previous system. At the start of the test, the pressure drops quickly at the top of the cell, down to approximately 6 bar. Because of this differential pressure (11.5 bar over 33 cm), a very slight amount of gas enters during the setting of the plaster. The pressure at the top of the cell rises again to 11.5 bar, and then drops down once more at approximately 28 hours. Throughout the duration of the experiment, the pressure measured at the top of the cell remained below the applied gas pressure. There has thus never been any gas communication between the bottom and the top of the cell, despite the differential pressures brought into play.

We can observe (Figure 6) the same type of behaviour at 5°C with another type of cement (LAFARGE, class A).

The right-angle set in a plaster/cement system is not, therefore, sufficient to oppose gas migration. The presence of microsilica is thus essential, in synergy with the cement and the plaster, for the particular applications contemplated.

The results given above bear witness to the remarkable properties of alpha plaster/ordinary Portland cement/microsilica systems for gas migration control during a cementing operation.

Once the system has set, it is also important for the integrity of the cement column to be maintained throughout the life of the well (several years). Now, plaster/cement systems are notorious for presenting longevity problems. Indeed, the sulphate ions contained in the plaster react chemically with the aluminate phases (C_3A) contained in the cement. The reaction product (ettringite) has a volume larger than the sum of the volumes of the initial components, which causes the system to expand. Excessive expansion is liable to lead to the formation of microcracks inside the material.

Figure 7 represents an expansion curve for a plaster/cement system in which a 2.5 % expansion of the sample is effectively observed after approximately five months. From the slope of the curve, it can be anticipated that there is a risk of this expansion continuing. On the contrary, the expansion of the system containing microsilica is limited to 0.4 %, which appears no longer to progress beyond 8 days. This particular phenomenon was not foreseeable.

TABLE 2

API Class A cement (40 % by weight)
alpha plaster (60 % by weight) (available from Lambert Corporation).
MICROBLOCK™ microsilica
Slurry density 1.89 kg/l

Microsilica weight %	Retarder weight %	Dispersing agent weight %	Rheology after mixing		Rheology at 15°C			TT^{iv} h:min	FL^{v} cm^3/30 min
			PV^{ii} Pa.s	YP^{iii} Pa	PV^{ii} Pa.s	YP^{iii} Pa	10 min gel Pa		
-	0.6	0.3	0.111	0.5	0.072	1.4	04.8	2:30	426
10	0.6	0.3	0.048	3.6	0.066	5.1	17.2	0:55	-
10	0.8	0.3	0.045	2.0	0.060	2.4	12.9	2:30	146
15	0.9	0.4	0.046	2.4	0.059	3.2	16.8	2:15	92
20	1.0	0.5	0.047	3.4	0.080	3.7	20.1	1:40	66
20	1.2	0.6	0.040	2.3	0.049	1.6	10.5	4:50	64
25	1.4	0.7	0.041	2.1	0.050	1.4	09.1	-	50

ii PV Plastic viscosity
iii YP Yield point
iv TT Thickening time
v FL Fluid loss

TABLE 3

API Class A cement (40 % by weight)
alpha plaster (60 % by weight) (available from Lambert Corporation)
MICROBLOCK™ microsilica (20 % by weight of plaster/cement mixture)
Slurry density 1.89 kg/1

Cement type	Retarder weight %	Dispersing agent weight %	BHCT[i] °C	PV[ii] Pa.s	YP[iii] Pa	Gel at 10 min Pa	TT[iv] h:min	FL[v] cm^3/30 min	CS[vi] 8 h kPa	CS[vi] 72 h kPa
CPA-HP	1.0	0.6	5	0.053	2.3	15.3	3:50	68	3437	10402
CPA-HP	1.1	0.6	5	-	-	-	5:20	-	-	-
CPA-HP	1.0	0.6	15	0.047	1.4	10.1	3:10	56	3108	14924
CPA-HP	1.0	0.6	25	0.040	1.7	09.6	4:30	-	3318	15421
LONESTAR	1.0	0.6	15	0.052	3.1	37.3	2:45	68	-	-
LAFARGE	1.0	0.8	5	0.068	2.7	22.5	3:20	72	3374	7651
LAFARGE	1.2	1.0	5	-	-	-	4:30	-	-	-
LAFARGE	1.0	0.6	15	0.057	2.9	33.5	1:55	64	3948	16177
LAFARGE	1.0	0.8	25	0.054	2.3	27.3	2:00	-	3185	13790

i	BHCT	Borehole circulation temperature
ii	PV	Plastic viscosity
iii	YP	Yield point
iv	TT	Thickening time
v	FL	Fluid loss
vi	CS	Compressive strength

TABLE 4

API Class A cement (40 % by weight)
GEORGIA PACIFIC alpha plaster (60 % by weight)
MICROBLOCK™ microsilica (20 % by weight of plaster/cement mixture)
Slurry density 1.89 kg/l

Cement	Retarder	Dispersing agent	BHCT[i]	PV[ii]	YP[iii]	Gel at 10 min	TT[iv]	FL[v]	CS[vi] 8 h	CS[vi] 72 h
type	weight %	weight %	°C	Pa.s	Pa	Pa	h:min	cm^3/30 min	kPa	kPa
LONESTAR	1.2	1.0	15	0.080	2.4	28.2	2:20	58	-	-
LONESTAR	1.3	1.0	15	0.082	2.4	35.0	3:15	56	2058	8792
LONESTAR	1.4	1.0	15	0.084	1.4	23.0	4:20	54	-	-
LAFARGE	1.3	1.0	15	0.089	2.6	36.9	2:20	60	-	-
LAFARGE	1.3	1.2	15	0.099	2.1	24.9	1:50	56	-	-
LAFARGE	1.4	1.0	15	0.112	3.6	36.9	2:10	66	-	-
LAFARGE	1.5	1.2	15	0.092	2.0	22.5	3:35	52	-	-
LAFARGE	1.4	1.0	25	0.081	2.4	27.3	2:45	56	3094	3423
LAFARGE	1.5	1.0	25	0.086	1.8	13.4	3:30	54	-	-

i	BHCT	Borehole circulation temperature
ii	PV	Plastic viscosity
iii	YP	Yield point
iv	TT	Thickening time
v	FL	Fluid loss
vi	CS	Compressive strength

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

1. A cement slurry composition for oil, gas, water, geothermal and analogous wells, comprising:

- cement;
- 66 to 150% alpha plaster by weight of cement;

  15 to 25% microsilica by weight of cement and plaster;
- 30 to 50% water by weight of cement and plaster.

2. A cement composition as claimed in claim 1, wherein the cement comprises ordinary API class A or C Portland cement.

3. A cement composition as claimed in claim 1 or 2, further comprising a setting retarder.

4. A cement composition as claimed in claim 3, wherein the setting retarder comprises calcium or sodium lignosulphonate.

5. A cement composition as claimed in any preceding claim, further comprising a dispersing agent.

6. A cement composition as claimed in claim 5, wherein the dispersing agent comprises a sodium/formaldehyde polynapthalene sulphonate retarder.

7. The use of a cement composition as claimed in any preceding claim for cementing an oil, gas, water, geothermal or analogous well having a temperature of 0 - 30 degrees C.

8. The use of a cement composition as claimed in claim 7, for preventing gas invasion into the well.

9. The use of a cement composition as claimed in claim 7 or 8 when applied to the cementing of surface casings.

FIGURE 1

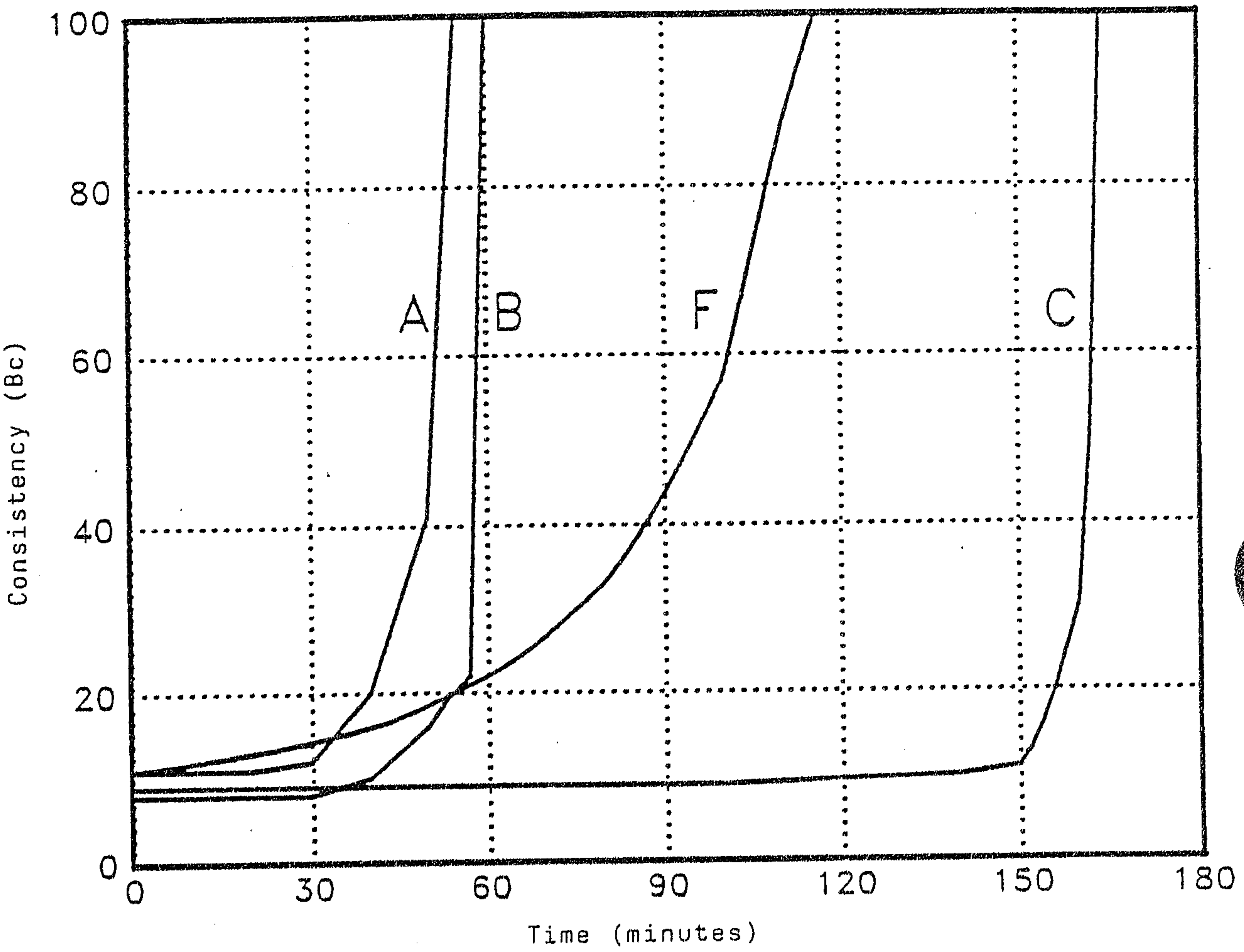


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FIGURE 2

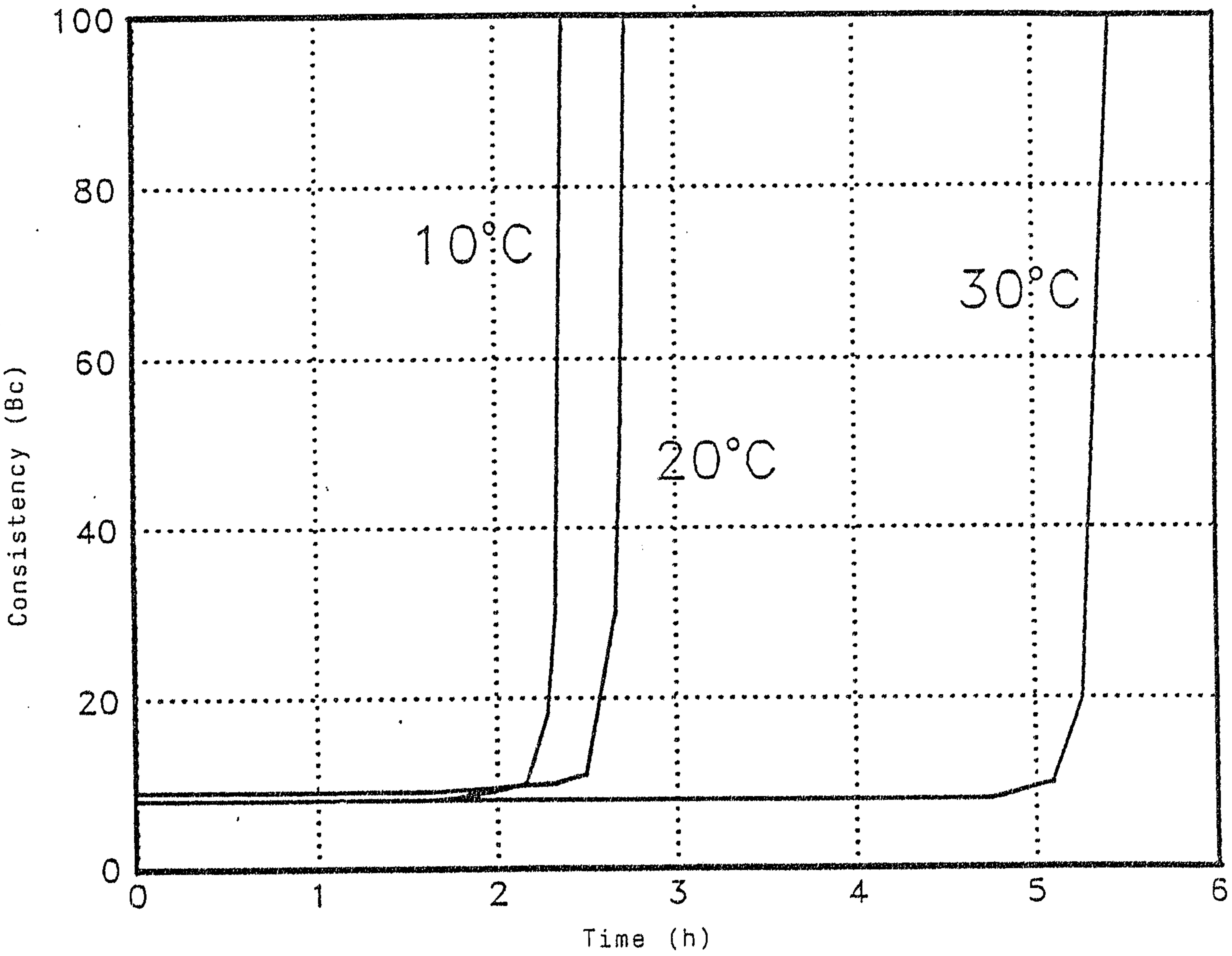

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FIGURE 3

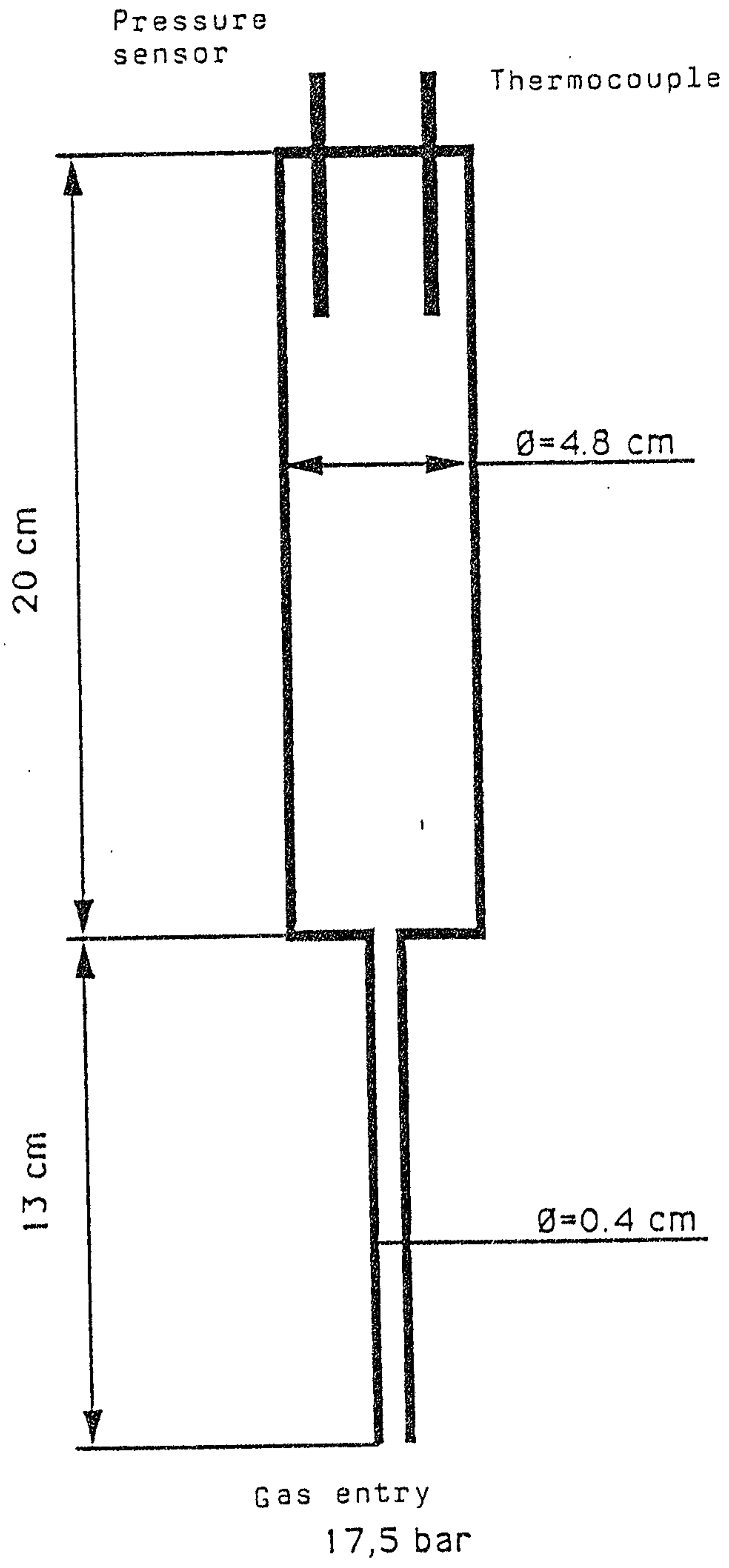

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FIGURE 4

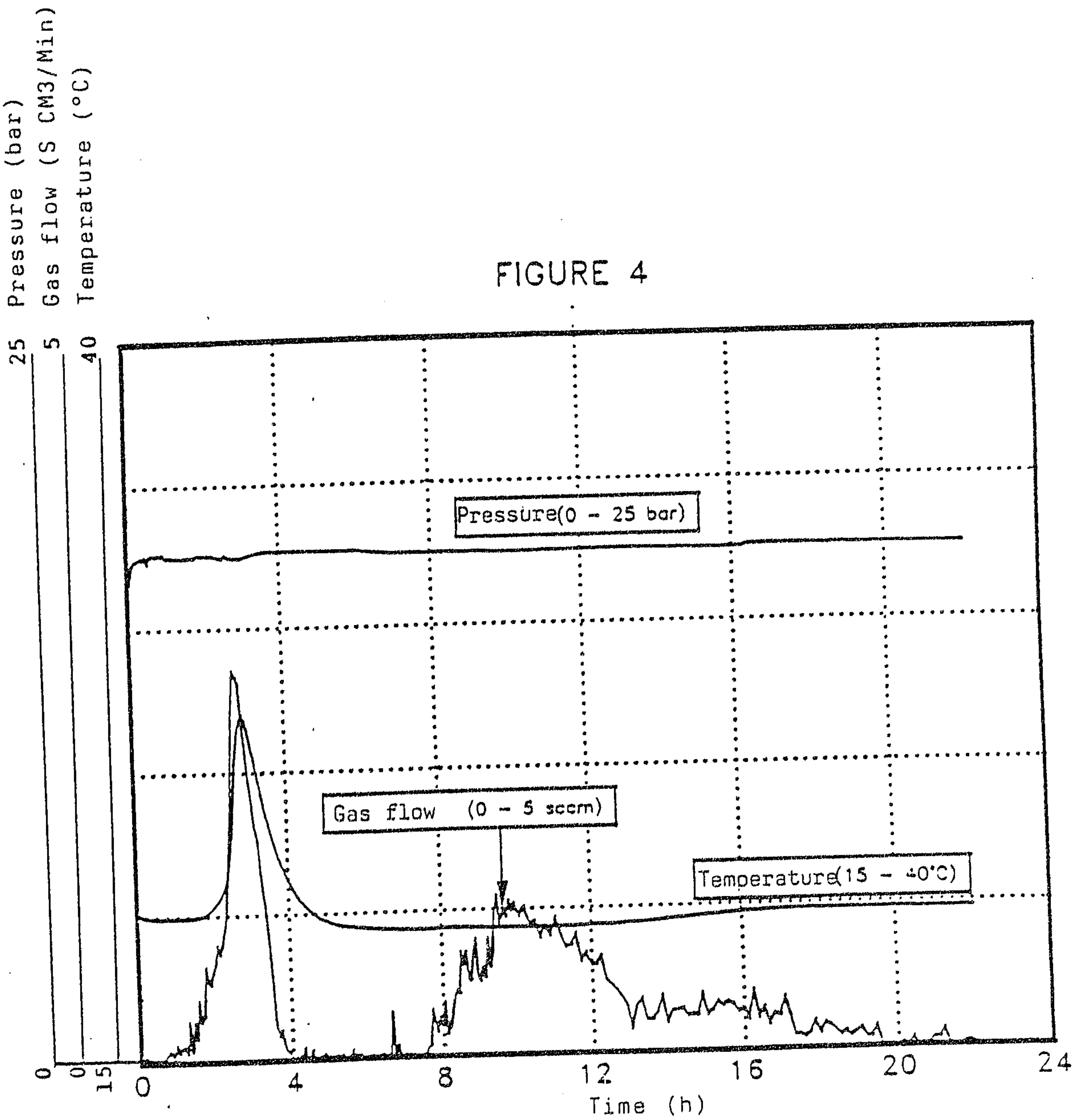

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FIGURE 5

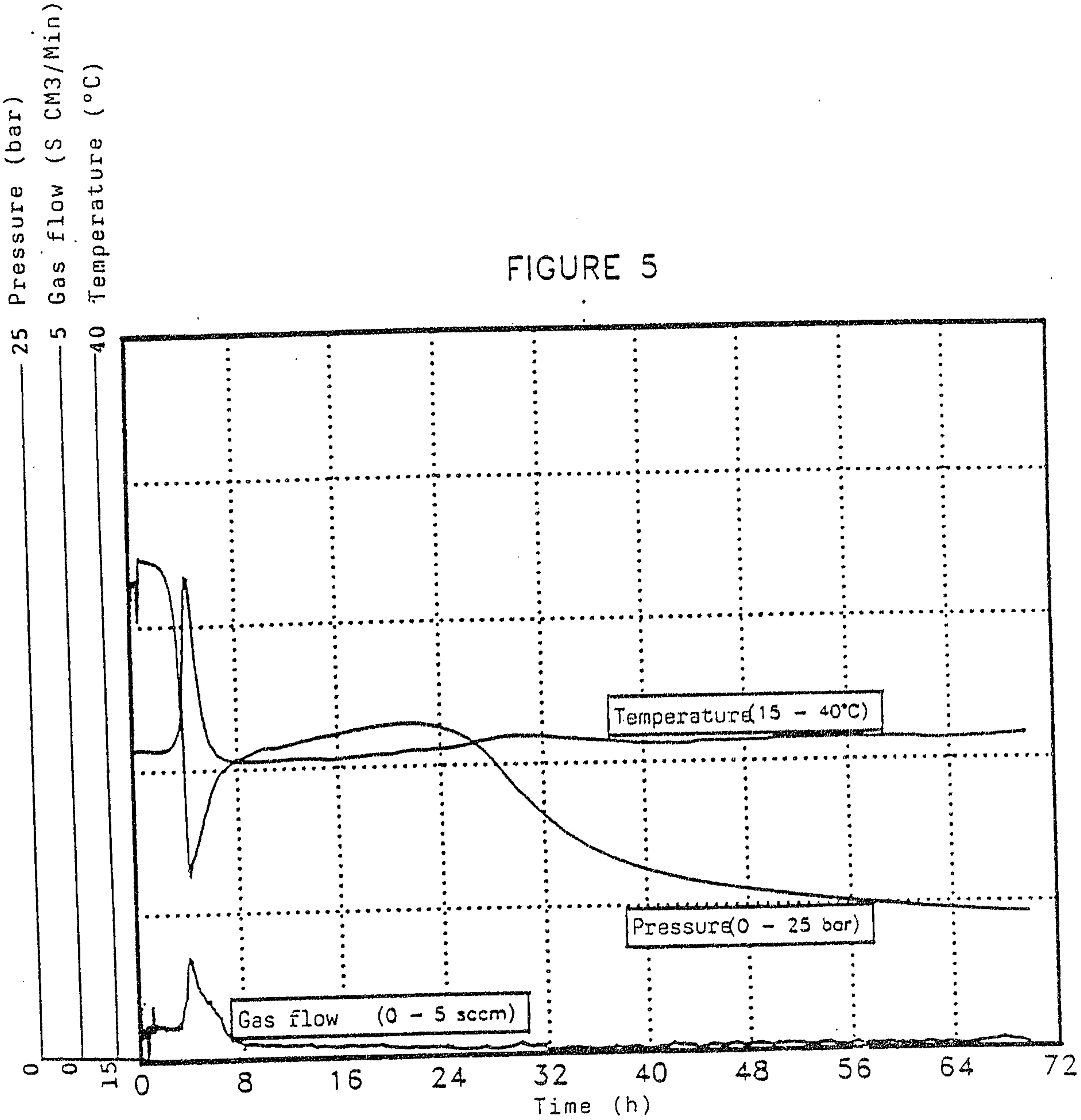

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FIGURE 6

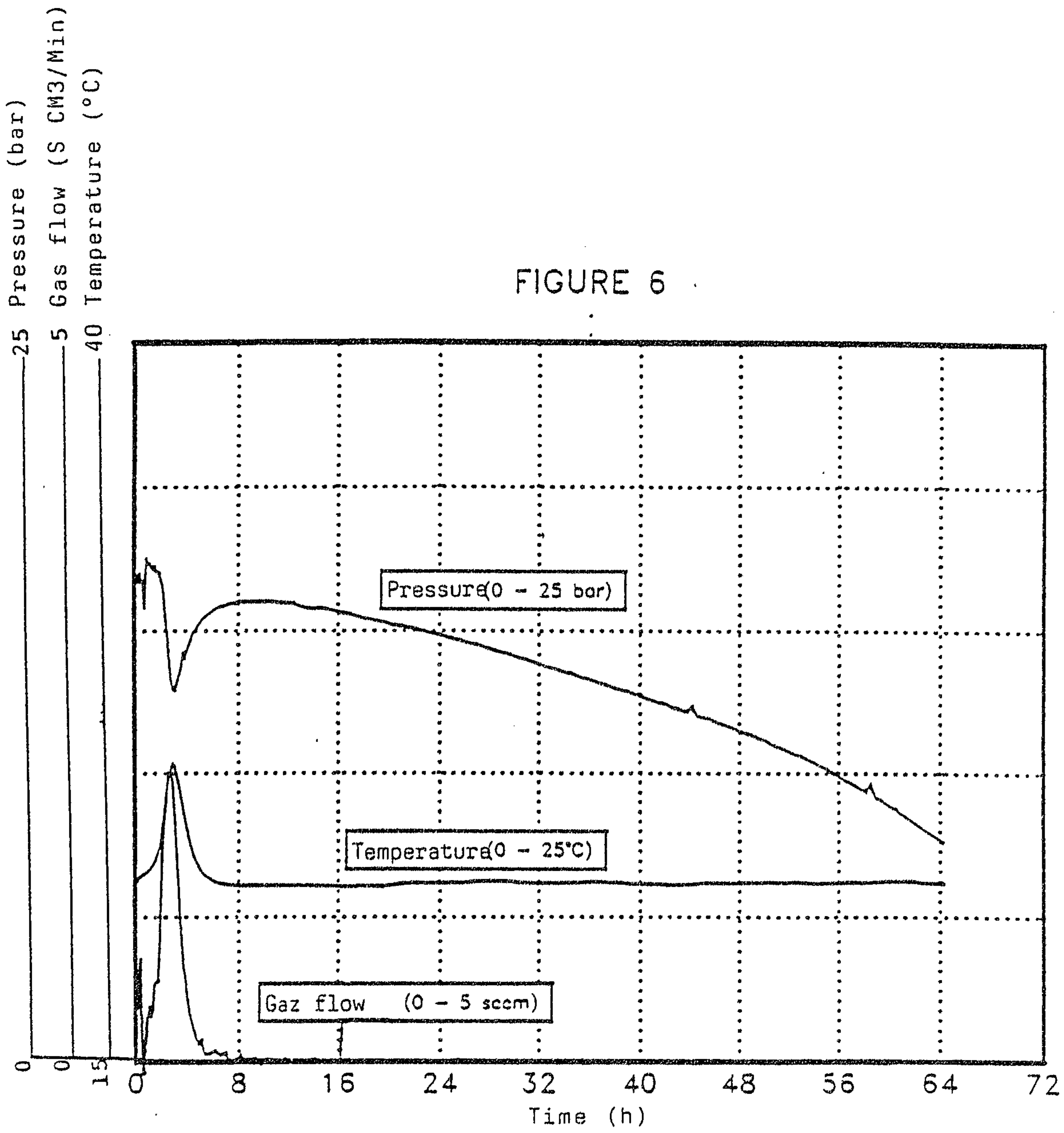

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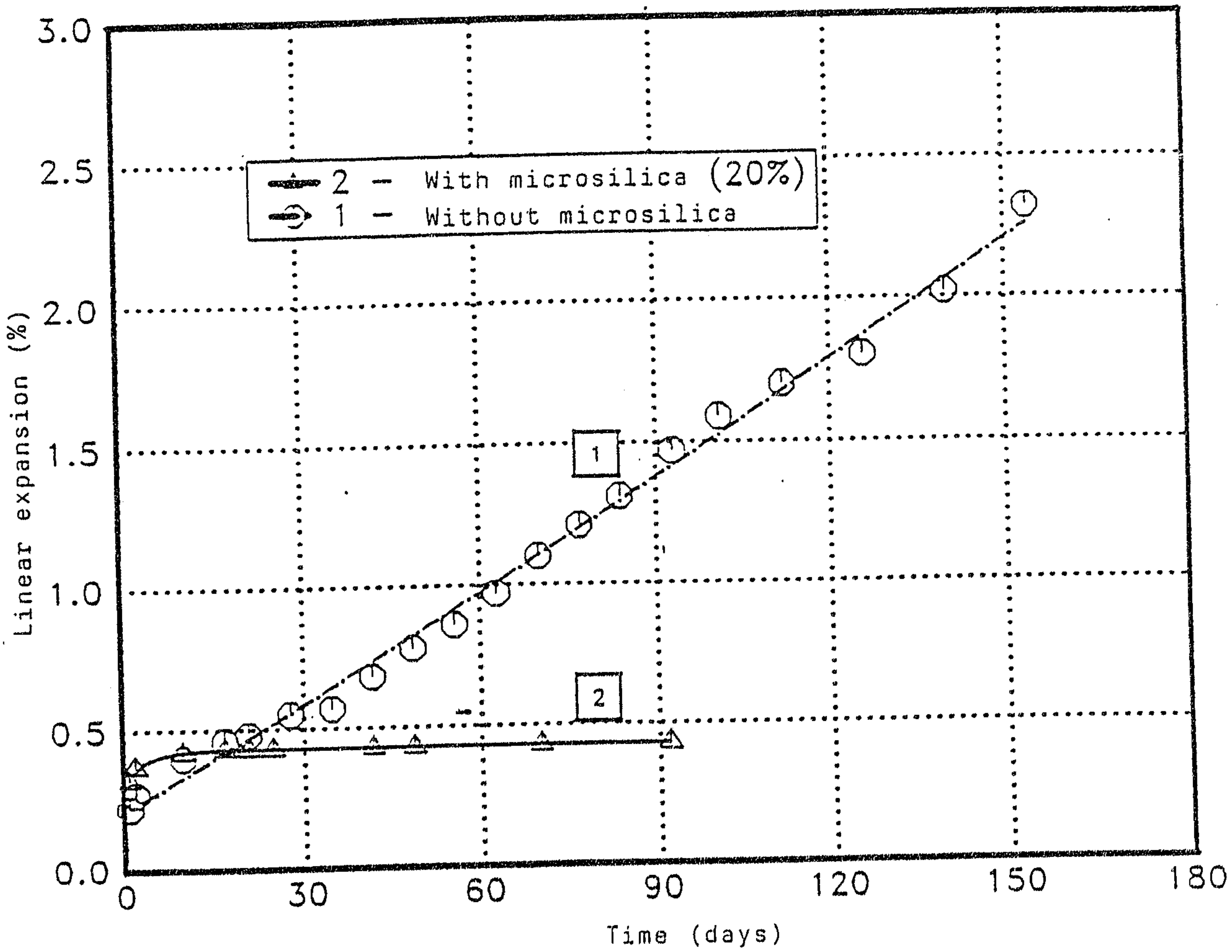
FIGURE 7



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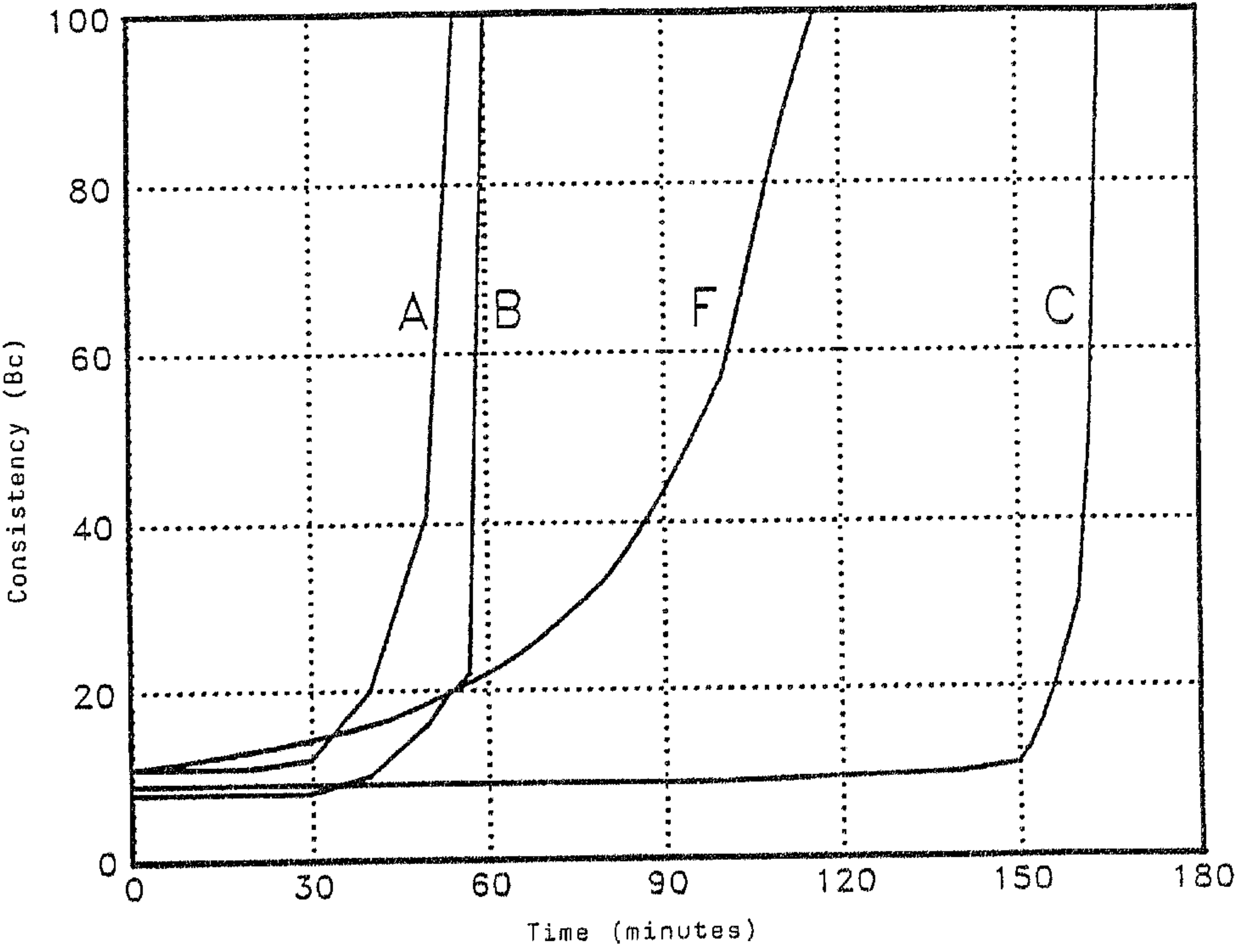
100
80
60
40
20
0
Consistency (Bc)
0
30
60
90
120
150
180
Time (minutes)
A
B
F
C