AAEC/ E58

AAEC/ E58

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

PURIFICATION OF CARBON DIOXIDE FOR REACTOR PURPOSES

PART I – LITERATURE SURVEY AND RECOMMENDED PROGRAMME

by

A. DRAYCOTT

A. C. KERR

First Issued Sydney, January 1960

Re-issued Sydney, February 1961

UNCLASSIFIED

AUSTRALIAN ATOMIC ENERGY COMMISSION

PURIFICATION OF CARBON DIOXIDE FOR REACTOR PURPOSES

PART I – LITERATURE SURVEY AND RECOMMENDED PROGRAMME

by

A. DRAYCOTT

A. C. KERR

ABSTRACT

The impurities likely to be present in carbon dioxide are listed; water is considered to be the most important in view of its adverse effect on the compatibility of many reactor materials with the gas. The literature on various desiccants is reviewed and a suggested experimental programme on drying of the carbon dioxide is outlined. Other major impurities are oxygen and nitrogen. Some chemical means for continually removing the oxygen appear possible. It is likely that the nitrogen content can only be lowered on charging the reactor; no continual method seems feasible at this stage. Minor impurities such as the oxides of nitrogen and sulphur are mentioned and the continual removal of dust in the coolant circuit is considered.

CONTENTS

FIGURE 1 Adsorption capacity as a function of relative humidity for the three desiccants.

1. INTRODUCTION

Because of its cheapness, availability and satisfactory heat removal properties, carbon dioxide has been the most favoured gaseous coolant used in nuclear reactors to the present time. Some temperature limitations exist because of the increasing incompatibility with certain popular reactor materials, particularly graphite, at temperatures which are desirable in order to yield sufficient advances over the Calder Hall type of reactor.

The A.A.E.C. have selected carbon dioxide as the preferable coolant in the development of an Australian High Temperature Gas Cooled Reactor (H.T.G.C.). A detailed compatibility programme is in progress in which the following systems are being studied:

(1) Beryllium – carbon dioxide, beryllium being selected as a canning material.

(2) Beryllia – carbon dioxide, beryllia being a possible moderator.

(3) The possible fuel and fertile materials UBe_{13} and $ThBe_{13}$ with carbon dioxide.

(4) Stainless steel – carbon dioxide. 18.8.1 stainless steel could be an alternative canning material and may also be used for structural purposes in the hotter parts of the system.

(5) Low alloy steels – carbon dioxide. The selection of structural materials for all parts of the circuit will be made on the results of these tests in conjunction with the desired mechanical and physical properties.

It is intended that the minimum gas temperature at the outlet from the reactor should be 500°C.

One of the most important variables to be studied in each of these systems is the impurity content of the gas. Already preliminary experiments have shown that any moisture in the gas could lead to higher corrosion rates with beryllium and possibly with 18.8.1 stainless steel.

A programme has therefore been initiated to develop methods to remove all impurities from the carbon dioxide so that compatibility tests with the pure gas can be carried out. It is intended that the fullest information should be obtained on all the developed processes so that a purification system for the reactor itself can be designed without any further experimental work.

2. THE RAW MATERIAL

The purest form of carbon dioxide available in Sydney is produced by a fermentation process. Although the purification system is a commercial secret it is known that the gas is dried by passing through concentrated sulphuric acid. The resulting moisture content is usually less than 50 p.p.m. The major impurity is air; in bottles the air content in the gaseous phase should not exceed 3.0% by volume, while in the liquid phase it should be less than 0.6%. However, the company supplying the gas can considerably reduce these figures. Because of variation in the quality of gas supplied in bottles it has been found preferable to install at Lucas Heights a bulk supply tank of 6 tons capacity.

The concentrations of impurities in the CO_2 supplied in bulk have been found to be: oxygen – approx. 10 p.p.m.; water – less than 50 p.p.m.

The only other impurities which are likely to occur are: sulphur dioxide – not exceeding 3 p.p.m. by weight; nitrogen oxides – not exceeding 0.1 p.p.m. by weight.

No carbon monoxide is present in the gas produced by the fermentation process. This differs from some of the gas used at Calder Hall which is prepared by the steam–coke process and which can contain appreciable quantities of carbon monoxide.

We are, therefore, concerned with the removal of the following impurities from the gas;

moisture,

oxygen,

nitrogen and

possibly sulphur dioxide and nitrogen oxides.

Equipment to supply carbon dioxide of specified purity on a laboratory scale must be developed and plant must be designed both to purify the coolant on charging the reactor and to continually maintain impurity levels below set limits during operation.

During circulation of the coolant it is likely that some dust from the moderator, and/or from scale formed on the surface of ducting and heat exchanger tubes may become entrained in the gas stream. Continual removal of this solid contamination is necessary and will be considered in the overall purification programme.

3. REMOVAL OF IMPURITIES

The removal of impurities will now be considered on an individual basis.

3.1 Moisture.

Moisture is one of the most troublesome impurities in that only very small concentrations lead to accelerated attack of many materials, particularly beryllium. Reduction of moisture concentrations to below 1 p.p.m. may therefore be necessary in order to operate a reactor with beryllium components at temperatures greater than 600°C (Munro and Williams, 1955).

Drying of gases has been studied by many investigators. Comparing liquid and solid desiccants Perry (1950) p. 878, states that although the equilibrium moisture content of liquid desiccants is often much greater than that of solid desiccants for the same gas, the solids have the advantage of yielding lower exit gas humidities. The solid materials have other advantages such as easier regeneration procedures and no entrainment of spray from liquid volumes. Therefore, the work on drying carbon dioxide will be limited to solid desiccants.

For many years silica gel and activated alumina have been the two most common solid desiccants used in industrial processes. Recently the group of materials known as molecular sieves has been developed. These highly selective adsorbents are rapidly being brought into use in many chemical process industries. Hence these three desiccants are the materials which will be studied in the carbon dioxide drying programme.

Most of the work on gas drying has been carried out on static beds. Adsorption on these fixed beds results in unsteady state conditions of mass and heat transfer. Fluidised beds would lead to greater efficiency but normally these gas adsorbents are difficult to fluidise. A U.S. Patent (2,834,429) has shown that molecular sieves can be fluidised if they are mixed with 1.5 times their weight of a finely divided material of the clay type and suitable size range. If this could be utilised on a large scale a new steady state gas adsorption technique would be available.

The following variables must be completely investigated in the gas drying programme.

(1) Inlet moisture content.

(2) Size of bed.

(3) Contact time, or velocity of gas in a bed of fixed size.

(4) Temperature.

(5) Pressure.

(6) Size and shape of desiccant particles.

(7) Regeneration.

The information pertinent to this study, with each of the three selected desiccants will now be considered.

3.1.1 Silica Gel

Almost all the information on the use of silica gel as a gaseous desiccant concerns air. Some data are available on hydrocarbons but few detailed results are reported for carbon dioxide.

The mechanism of silica gel drying has been described by many workers. Most regard the pores of the material as multiple connecting capillaries of various diameters. The initial vapour condensing in the pores is essentially a monomolecular layer which will form even at very low relative humidities. Further adsorption is in the form of capillary attraction with the pores filling up in proportion to the relative pressure of the adsorbed vapour. The condensed liquid in the capillary forms a meniscus concave to the vapour phase. The vapour pressure over this meniscus is lower than the normal vapour pressure of the liquid by an amount proportional to the degree of curvature. Hence in small capillaries, such as the narrower sections of the pore channels, vapours can condense at pressures far below the normal vapour pressure. Small diameter pores therefore give larger lowering of the pressure, resulting in more adsorption at low relative pressures. As the relative pressure increases, adsorption in the larger radius pores takes place.

Most of the variables mentioned above have been studied closely for an air system. As expected, greater useful capacity (defined as a measure of the total moisture adsorbed by a bed of desiccant up to the time it becomes saturated and loses drying efficiency) is obtained with deep beds than with shallow beds under any set of operating conditions. The gas velocity of approximately 60 ft/min is usually quoted (W.R. Grace, 1958) as suitable for most equipment although for very low dew points velocities of 20 to 40 ft/min are preferred.

Higher temperatures cause lower useful capacities. This also results in limited exit dew point where there is a large temperature rise through the bed. It is therefore occasionally necessary to dissipate the heat of adsorption by cooling coils or other convenient means, or alternatively by operation at elevated pressures.

Equilibrium data for silica gel and water have been obtained by both static and dynamic methods over a considerable range of relative humidities at room temperature (20°C). Dehler (1940) and Taylor (1945) have provided more comprehensive information by extending the known data to a temperature range of −18 to +200° C. In his work at low relative humidities Taylor (1945) showed that the adsorption capacity (expressed on a weight basis) of silica gel is very low at all temperatures with inlet dew points below 0° F, and at temperatures higher than 60°C where the inlet dew point is below 53°F.

The data obtained is presented in the form of a Cox's Chart or isosteres which can be expressed as (Hougen, Watson and Ragatz, 1954)

$$\frac{p}{p_o} = at + b$$

where p = partial pressure

p_o = saturation pressure

t = temperature

and a and b are constants depending on the useful adsorption capacity. It is found that a increases while b decreases as the useful capacity increases. These isosteres also indicate that over a limited range the adsorption capacity at a given $\frac{p}{p_o}$ is virtually constant.

Hubbard (1954) working with Davison silica gel, showed that under optimum conditions the outlet air could be dried to a dew point as low as -80°F. He produced equilibrium curves down to a dew point of -36° F but conceded that the ones shown below this figure were subject to some doubt.

Blower (1944) further lowered the dew point of the outlet gas by drying at elevated pressure and then allowing the gas to expand to atmospheric pressure. Values that can be obtained after drying at 100 p.s.i.g. can be as low as -100 to -108°F dew point, measured at atmospheric pressure. Obviously this technique is not suitable for a pressurised reactor circuit.

Over the range of relatively high humidities, (circ. 30–70% R.H.) Patrick (1930) showed that the adsorption of vapour is on a volume basis by the following relationship:

$$V = K \left(\frac{p\sigma}{p_o}\right) \frac{1}{m}$$

V = volume of liquid adsorbed

σ = surface tension of liquid

K and m are constants

Vapours discussed here can be many; commercially, silica gel is used for selective adsorption of hydrocarbons from natural gas, aromatics from paraffins, fluorine from HCl to mention but a few.

The particle shape and size are not so important as other variables. Small particle size and irregular granular shape permit the most effective contact between gas and desiccant resulting in greatest efficiency. The smaller size also leads to higher pressure drop and so the design for any specified purpose is a compromise between the two conflictions.

Silica gel is easily reactivated by heating to an elevated temperature, 165°C being adequate for most purposes. On no account should the heating be allowed to exceed 315°C as the desiccant capacity will be adversely affected.

Counter current reactivation is usually used to ensure maximum activity at the outlet end of the bed. For low dew points cocurrent air or gas is desirable but on grounds of simplicity and economy counter current cooling is generally employed. A very recent innovation on regeneration procedures has been reported by Boucher (1959). He claimed much more rapid and better results can be achieved using ultrasonics. This also applied to alumina and activated carbon.

3.1.2 Activated Alumina

Little detailed information is available on the use of alumina as desiccant for carbon dioxide, most of the work having been with air. However, alumina is used as the desiccant in the units on the Calder Hall circuits. In a private communication dated 1959 Nairn stated that the normal moisture content in the gas is less than 25 p.p.m., but there are occasions, for instance during start-up, when this value is exceeded temporarily and may be above 100 p.p.m. until the driers exercise their full effect during gas recirculation.

Hartog (private communication, 1959) has provided more detailed information about the units themselves. There are two towers containing activated alumina which are operated in turn so that one is being re-activated while the other is taking up water from the circuit. The capacity of the plant is sufficient to remove continuously 1.25 lbs of water vapour per hour with the gas at 100 p.s.i.g. and a temperature of 140°C.

The average flow rate through the towers under the conditions stated is 100 cu. ft. per minute with a differential pressure of 4 p.s.i. The normal operating temperature of the alumina is 25°C and during reactivation the temperature is raised by passing heated gas over the alumina pellet surface until they reach about 325°C, after which the gas is cooled down to 25°C when it gives out most of its water which is removed by a cyclone type separator. The normal period for a complete cycle is eight hours.

The isothermal dynamic adsorption of water vapour on activated alumina was studied by Eagleton (1951). He found that over a range of 2–50% relative humidity of the inlet gas this relative humidity observes a linear relationship with the percentage of moisture adsorbed down to a dew point of −30°F. This range of humidities was extended to 80% relative humidity, by Miller and Roberts (1958) using British activated alumina and found the linear relation still to hold. It was also shown that the adsorptive capacity was independent of the absolute humidity at constant relative humidity.

While Eagleton (1951) reported that at a relative humidity of 12% no variation in capacity with flow rate existed over the range 0.9–4.3 lb/(min)(ft^2), Miller and Roberts (1958) noticed some variation with flow rate at much higher humidities (70%). Some of their results are reproduced below.

TABLE 1

Relationship between flow rate and adsorption capacity

Rate of Flow lb/(min)(ft^2)	Average Bed Relative Humidity %	Adsorption %
3.3	71	10.7
4.2	74	9.2
5.1	69	9.2
6.2	71	7.1
7.0	69	7.4
8.3	65	7.7
9.8	69	6.2

At low inlet humidities the useful capacity is correspondingly low, although outlet dew points of -100° F are easily obtainable at room temperature. Such low outlet figures reported at higher temperatures in isolated cases have not been substantiated.

Miller and Roberts (1958) also studied the effect of regeneration at different temperatures. As would be expected, increase in the reactivation temperature increases the adsorption capacity. Some results are given below.

TABLE 2

Relationship between reactivation temperature and adsorption capacity

Temperature of Reactivation $^{\circ}$F	Relative Humidity %	Adsorption %
390	69	11.4
570	65	13.5
756	69	17.3

Perry (1950) stated that 600° F is the recommended temperature for industrial applications.

Using Ergun's (1952) method for fluid flow through packed beds, Perry correlated pressure drop data for alumina driers in the form

$$\frac{\Delta P}{L}\frac{g}{GV}\frac{D_p}{}\frac{\epsilon^2}{1-\epsilon} = F_L$$

where ΔP = pressure drop lb/ft^2 .

g = acceleration due to gravity ft/sec^2.

L = height of bed (ft.) .

D_p = diameter of equivalent volume sphere (ft.) .

G = mass rate of flow (lb/ft^2 sec).

V = linear rate of flow (ft/sec) .

ϵ = fractional void volume

F_L = function of the modified Reynolds number. $Re^1 = \frac{D_p G}{\mu(1-\epsilon)}$

μ = viscosity (lb/ft sec).

This correlation is not solely for alumina. Before such a correlation was suggested, use was made of the specific curves for size fractions, Mantell (1951), p. 90, and with pressure as a parameter, Mantell (1951), p. 393.

3.1.3 Molecular Sieves

In recent years the group of materials known as molecular sieves have become widely used as highly selective adsorbents for many gases. In particular molecular sieves have been used as desiccants for many gases. Barrer (1959), one of the most consistent workers in this field has discussed the structural aspects in some detail. The zeolites were the first group of compounds to come into this classification. When the natural crystal water is removed from this type of substance a porous crystal is obtained, the pore systems of which consist only of channels of molecular dimensions, these dimensions being quite precise and controlled as accurately as the positions of the lattice atoms surrounding them. These dimensions can vary somewhat along the length of a channel but the periodicity is perfectly regular. Molecules which are of the wrong shape and size would be totally unable to penetrate into the crystal; others of similar size or smaller might penetrate readily and would then under appropriate conditions of pressure and temperature saturate the crystalline free volume of the porous crystals.

The Linde Company of the U.S.A. has been one of the companies foremost in production of these materials and pioneering their use in industry. They are producing two kinds of sieves which are currently being used for gas drying. These are Type 4A which will admit molecules up to 4 Angstroms in diameter to enter the adsorption cavities and Type 5A which will accept molecules up to 5 Angstroms in diameter.

Table 3 lists the critical diameters of some of the more common gas molecules.

TABLE 3 *

Critical diameters of selected gas molecules

Molecule	Critical Dimension ^{o}A
H_2	2.4
O_2	2.8
He	$\sim$ 2.8
N_2	3.0
A	3.8

* The critical dimensions are given by Barrer (1959) and calculated using bond distances and Van der Waal's atomic radii.

Because of this size factor in molecular sieve adsorption in some gas drying operations, it is not unusual to find that other components of the gas stream are being adsorbed in addition to water. However, because molecular sieves have an extremely high adsorptive attraction for water, it is found that the water molecule will normally displace any other material that is already adsorbed on the molecular sieves. In this case some partial reduction in the adsorption capacity and rate of adsorption is encountered.

This coadsorption is a feature of the CO_2 water system which has not been studied for molecular sieves.

It has already been indicated (Sections 3.1.1 and 3.1.2) that optimum performance of silica gel and alumina is obtained with high inlet relative humidities of 30% and over but as shown in Figure 1 (from Linde, 1958) the molecular sieve performance is exceptionally good even below 5% relative humidity.

A further important feature of the molecular sieve type of desiccant is the ability to effectively dry gases at elevated temperatures. This is particularly important in a reactor system where loss of heat necessitated by low temperature drier operation must be kept to a minimum. Molecular sieves have been used in some cases up to 200° C.

Regeneration of the sieves has to be carried out at a fairly high temperature because of their high retentivity of the water. Usually for water desorption a temperature of the order of 300°C is recommended although the materials can be heated to 500°C without undergoing serious damage.

The Linde Company (1958) bulletin also supplies some information on the effect of gas velocity through the bed. A linear relationship apparently exists between the capacity at "break through" point and the superficial linear velocity.

i.e. $w = av + b$

where a and b are constants such that a is small and less than zero. The capacity is thus constant over a large range of superficial velocity.

There is obviously an outstanding lack of data on the use of molecular sieves for drying carbon dioxide, although even at this stage, significant improvements on the performance of alumina or silica gel driers can be expected.

3.2 Oxygen

Oxygen is present in the carbon dioxide as a constituent of air introduced at various stages of the fermentation, purification and compression process. The effect of oxygen as a contaminant in the carbon dioxide on the compatibility properties has not yet been determined. The Calder Hall gas does not contain very much air and no attempts are made to limit the concentrations of either oxygen or nitrogen in the circuit.

At the higher temperatures envisaged for the Australian H.T.G.C. reactor the possible effects of oxygen on the corrosion of all reactor materials must be evaluated. Little information is available on the removal of oxygen from carbon dioxide, but considerable research has been carried out on the removal from inert gases particularly for glove box application. In those cases the oxygen is usually reacted with metals at elevated temperatures. Calcium at 400° C, copper at 600° C and NaK at 180° C are among the favoured methods. Gibbs, Svec and Harrington (1956) have studied the use of fifteen metals in removal of oxygen and in some cases nitrogen from the inert gases. Efficiency temperature data are supplied for each material. Usually temperatures of the order of 600°C are preferred for oxygen removal; at these temperatures each of the metals suggested would also react with carbon dioxide.

One of the most common methods of removing oxygen from argon is by the use of reduced pyrolusite at a temperature of 150–180°C. (Smith and Sheridan, 1958). It is quite feasible that these lower oxides of manganese will also react with the carbon dioxide at these temperatures to give either the carbonate or basic carbonate but this reaction is likely to be subservient to the $MnO–O_2$ reaction. The use of reduced pyrolusite for oxygen removal should therefore be fully investigated. Regeneration of the pyrolusite is carried out by passing hydrogen countercurrently at a temperature of 300° C; unfortunately the bed capacity is reduced to some extent after each regeneration.

A further method for removing oxygen has been developed recently by Schütze (1958). He prepared an active copper catalyst which would react with oxygen but not carbon dioxide at temperatures around 150° C. He claimed that the removal of oxygen from nitrogen and rare gases down to 0.1 p.p.m. is possible at 20° C with the catalyst in the reduced form, while at 95°C sulphur compounds could be removed from carbon dioxide. This material is therefore worthy of a complete study for removal of oxygen and oxides of sulphur from carbon dioxide.

A U.S. patent (U.S. 2,810,454) describes a process developed by Union Carbide's Linde Company to remove from gaseous argon 2% oxygen using molecular sieves; the resulting argon has an average total impurity content of 13 p.p.m. The adsorption is carried out on a feed from an air distillation plant at a pressure slightly above atmospheric and a temperature a few degrees above the saturation temperature of the argon oxygen mixture, i.e., −180 to −175°C; a contact time of 30 seconds is sufficient. Regeneration of the sieves is done by waste nitrogen from the distillation process at ambient temperatures.

3.3 Nitrogen

It is unlikely that nitrogen will have any deleterious effect on the compatibility of carbon dioxide with any of the reactor materials contemplated in the Australian H.T.G.C. reactor. However, the concentration should be limited in the reactor circuit as the (n,p.) reaction yielding the β emitter C14 could be troublesome. We should also be able to produce carbon dioxide with very low nitrogen contents for some compatibility experiments. It is therefore necessary to make some investigations into the problem of nitrogen removal.

Carbon dioxide is usually more reactive towards most materials than nitrogen and hence chemical methods for removing the nitrogen are difficult if not impossible to develop. The present chemical methods of nitrogen removal from inert gases, e.g. use of calcium metal at 400–500°C, are completely unsuitable for carbon dioxide. The possibility of oxidising the nitrogen to the varying oxides of nitrogen exists, but this introduces the problem of completely removing these gases. In the presence of any water vapour nitrous or nitric acids could form which would be far more detrimental than the original parent nitrogen.

At the temperature and pressure of the bulk liquid carbon dioxide, 300 p.s.i.g. and 0°F, nitrogen is a permanent gas and therefore exists in solution in the liquid phase. Thus any operation to reduce the solubility will be beneficial, e.g. increase in temperature or reduction in pressure; the amount of nitrogen released is limited by the vapour liquid equilibrium curve for carbon dioxide. Unfortunately, any such method has a considerable carbon dioxide wastage.

The nitrogen content could be reduced by this method on charging the reactor, the final concentration being decided by the conflicting demands of low nitrogen content selected, or maximum C14 concentration, and minimum wastage of carbon dioxide.

3.4 Oxides of Nitrogen and Sulphur

A number of methods exist for the removal of these contaminants. However, because of their extremely low concentration in the gas supplied and the very low probability of any formation of these poisons in the circuit, no further mention will be made of this problem and their removal will not form part of the experimental programme in the first instance.

3.5 Dusts

The types of dusts encountered in gas cooled reactors are in no way similar to the "atmospheric dusts" met in air conditioning plants and as a result the problems are completely different. The dust source arises from compatibility problems between the coolant gas and the reactor structural and canning materials. Depending on the reactor system the dusts could contain graphite, beryllia, oxides of iron, and the oxide of the fuel can material (e.g. magnesium). The main difficulty in any examination of the problem is that the nature of any dust which may be created is largely unknown with no exact specification of the particle size.

Filters of various types and incorporated into different parts of the coolant circuit may be employed to remove the dusts. Froggatt (1959) has recently described a new filter satisfying the more stringent demands in this type of circuit.

3.5.1 By–pass Unit

A by–pass unit providing continuous filtration of a small percentage of the main stream may be used to maintain the circulating gas free from dust build–up. Because the gas is continually recirculated, efficiency requirements are not so stringent as some other applications; 95% by weight of 10 micron particles is the minimum.

3.5.2 By–pass Filter on Gas Purification Circuit

This type of filter is also continuous and has the advantage of preventing dust contamination of the gas driers and any other purification units which may be incorporated. The efficiency requirements are similar to the by–pass filter described in Section 3.5.1 but because of the other units in series the pressure drop allowed through the filter is critical, and usually limited to 1 to 2 p.s.i.g.

3.5.3 Relief Valve Filter

If it is not considered necessary to continually filter the recirculating coolant it is always desirable to prevent the discharge of any radioactive dust into the atmosphere should pressure build up in the circuit cause a relief valve to blow. The conditions for such a filter attachment are stringent, the filter having to handle with equal efficiency a variable flow ranging from full to leak flow of the safety valve which has not reseated correctly. It is recommended that this unit should be almost 100% efficient at dust sizes of 10 microns with good efficiencies down to 2 microns.

3.5.4. Types of Unit

Filter units which have been considered are ceramics, porous stainless steel and materials such as fibreglass, but each have defects which are not acceptable for their exclusive use. The proven performance of cyclones has caused considerable research to be done in this sphere resulting in appropriate cyclones being designed for each of the conditions mentioned above. Le Page (1959) has reported that some of these units have now been tested under operating conditions and results on the Bradwell drier circuit filters show that efficiencies of 99.5% by weight can be obtained with dusts 100% < 13 microns, and 8% < 5 microns.

4. CONCLUSIONS AND RECOMMENDED PROGRAMME

Although purification circuits have been included in most carbon dioxide cooled reactor systems, little information is available for the design of units to remove specific impurities to particular levels. Indeed most of the effort has been directed towards drying the gas, and although much dehumidification data is available for air no systematic study with carbon dioxide has been completed. It is therefore proposed to study the three recommended desiccants, alumina, silica gel and molecular sieves with carbon dioxide and to fully investigate the effect of all the variables listed in Section 3.1 on the performance of each.

Two methods for the removal of oxygen, the use of reduced pyrolusite and the activated copper catalyst are being studied. Again, experiments will be carried out to determine the effect of each of the complete list of physical variables.

Some theoretical considerations on nitrogen removal and a paper study of the conditions for charging the reactor circuit will be completed in the proposed programme.

It is not envisaged that any work on the trace impurities, sulphur dioxide and oxides of nitrogen will be included in this study. However, if the problem is deemed important, experiments on dust removal, particularly associated with the dusts likely to be encountered in the H.T.G.C. reactor will be carried out.

When this work is completed it is expected that sufficient information will be obtained to design experimental units providing gas of any purity required for compatibility programmes. Also, the full design and cost estimation of the complete purification of the coolant on the reactor circuit will be possible from the data obtained.

BIBLIOGRAPHY

Addison, C.C., Iberson E. and Raynor, J.B., 1958. Use of Molecular Sieves to Maintain Clean Surfaces on Liquid Sodium and Liquid Bismuth. Chem. and Ind. January 25.

Barrer, R.M., 1959. New Selective Sorbents: Porous Crystals as Molecular Filters. Brit. Chem. Eng. 4: 267.

Blower, J.J., 1944. Revised Results Obtained with Certain Dehydrating Agents Used for Drying Gases. J. Research Nat. Bur. Standards 33: 199.

Boucher, R.M.G., 1959. Ultrasonics Boosts Heatless Drying. Chem. Eng. September 21, 1959, 66: 151.

Brit. Chem. Eng., 1957. Advances in Purification of Inert Gases, 2: 424 .

Cardorette, W. and Zall, D.M., 1958. Linde Molecular Sieves as Dynamic Dehumidification Desiccants, EES-010327.

Dehler, F.C., 1940 Silica Gel Adsorption. Chem. and Met. Eng. 47: 307.

Draycott, A., 1958. Compatibility of Steels with Carbon Dioxide. Internal report AAEC/K255.

Eagleton, L.C., 1951. Drying of Air in Fixed Beds. Dissertation Yale School of Engineering.

Ergun, S., 1952. Fluid Flow through Packed Beds. Chem. Eng. Progress 48: 89.

Froggatt, P.J., 1959. Filtration in Reactor Gas Circuits. Nuclear Engineering, Nov. 1959, p. 406.

Gibbs, D.S., Svec, H.J. and Harrington, R.E., 1956. Purification of the Rare Gases. Ind. Eng. Chem. 48: 289.

Grace, W.R. and Co., 1958. Adsorption and Dehydration with Silica Gel. Technical Bulletin 202. Davison Chemical Division .

Hougen, O.A., Watson, K.M. and Ragatz, R.A., 1954. Chemical Process Principles, Vol. 1. John Wiley, New York.

Hubbard, S., 1954. Equilbrium data for Silica Gel and Water Vapour. Ind. Eng. Chem. 46: 356.

Jones, R.A., Milton, R.M., 1954. Argon Purification. U.S. Patent 2,810,454,

Kinsella, A.J., Dickens, S.P., Ballard, W.P. and Smith, B.F., 1958. Fluidization of Adsorbents for Gases. U.S. Patent 2,834,429 (May 13, 1958).

Le Page, R.C., 1959. Dust Removal in Gas Cooled Reactors. Nuclear Power 4 (36) : 104.

Linde Company, 1950. Dry Gas. Technical Bulletin. Linde Molecular Sieves. Division of Union Carbide Company.

Mantell, C.I., 1951. Adsorption – 2nd ed. McGraw–Hill, New York.

Miller, A.W. and Roberts, C.W., 1958. The Drying of Gases with Activated Alumina. Ind.Chem. 34, (397) : 141.

Munro, W. and Williams, J., 1956. The Reactions of Beryllium with Carbon Dioxide in the Temperature Range 500–700°C. AERE M/M108.

Patrick, W.A., 1930. Adsorption of Vapours. Colloid Symposium Annual 7: 192.

Perry, J.H., 1950. Chemical Engineers' Handbook, 3rd. ed. McGraw–Hill, New York.

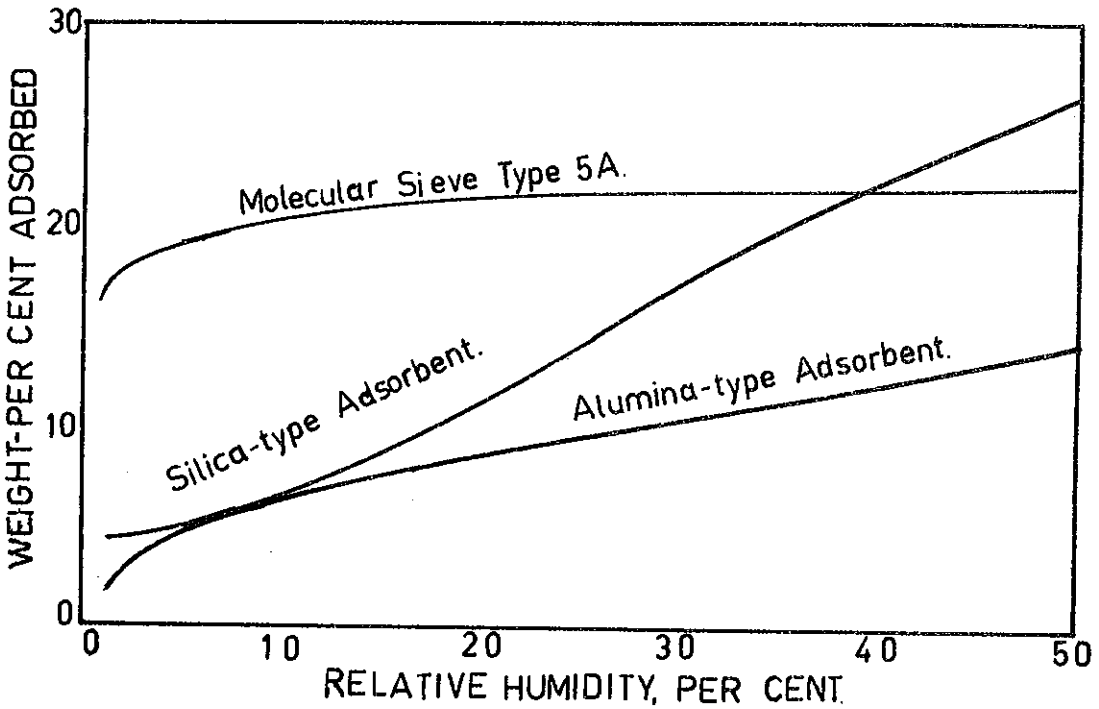
Schütze, M., 1958. Use of Activated Copper Catalyst for Removal of Oxygen from Gases. Angew. Chem. 70: 697.

Smith, S.E. and Sheridan, M.B., 1957. The Design and Operation of High Purity Inert Atmospheric System. Symposium on Glove Box Design and Operation. AERE GBS/17.

Taylor, R., 1945. Water Adsorption Measurement on Silica Gel. Ind. Eng. Chem. 37 : 649.

Timms, D.G., Konrath, H.J. and Chernside, R.C., 1958. Determination of Impurities in Carbon Dioxide by Gas Chromatography with Special Reference to Coolant Gas for Nuclear Reactors. Analyst 83: 600.

Wilson, B.J., 1958. Molecular Sieves. A Literature Survey. AERE Inf./Bib. 116.



ADSORPTION CAPACITY AS A FUNCTION OF RELATIVE HUMIDITY FOR THE THREE DESICCANTS (from Linde, 1958)

FIG. 1.