# CURRENT METHODS AND POTENTIAL SYSTEMS FOR PRODUCTION OF CONTROLLED ATMOSPHERES FOR GRAIN STORAGE

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Abstract: In controlled atmosphere storage, the atmosphere around the stored grain is modified to give an environment rich in $CO_2$ (> 40%) or low in oxygen (< 1%). At present tanker-delivered liquified gases (nitrogen or $CO_2$) are usually used to create these atmospheres but there are several other processes which appear suitable. These include pressure swing absorption systems, burners fueled with propane, producer gas, biogas or hydrogen, various forms of enhanced hermetic storage systems, fermentation processes and electrolytic or photolytic oxygen removal systems. Many of these techniques utilise materials available from sources close to or at the storage site, a major advantage over tanker delivered gases which may have to be transported over long distances from point of production. The rates of supply required to create and maintain five possible atmospheres are given. The atmospheres considered are low oxygen systems (< 1%) in nitrogen, or nitrogen/$CO_2$ mixtures, high-$CO_2$ (> 70%) and intermediate-$CO_2$ (ca 40%) mixtures, and atmospheres similar to those found in hermetic storages (< 6% $O_2$, > 14% $CO_2$). The various potential techniques of gas production are discussed in terms of their mode of operation, fuel and electricity requirements, scale of application and capital cost. It is concluded that on-site processes for gas generation should generally supersede use of tanker delivery and that eventually controlled atmospheres could be generated by a controllable form of the ancient hermetic storage technique.

## 1. INTRODUCTION

Controlled atmosphere (CA) treatment is now an established technique for the protection of stored grain. It is in limited commercial use in several parts of the world: e.g., Australia (Banks *et al.*, 1980), China (Champ *et al.*, 1982), Italy (Tranchino *et al.*, 1980) and continues to attract development interest in others: e.g., Bulgaria (Stoyanova and Shikrenov, 1979), Nigeria (Adesuyi, *et al.*, 1980), USA (Jay, 1980) and USSR (Anon., 1974). There are three major impediments to its more widespread adoption: the need for well-sealed storage, the long exposure times required for complete effectiveness and the lack of cheap convenient methods for supplying the gases required. Methods for provision of suitability modified storages are currently receiving much attention and with considerable success (e.g. see papers in this conference). The long exposure time appears to be an inherent restriction of the technique. This paper is aimed at illuminating and, perhaps, providing some of the ideas that may help to remove the third impediment, the lack of appropriate methods of gas supply. The discussion is largely limited to the use of CA for insect control in dry grain (< 12% moisture content) although the principles involved in the gas generation systems can usually be extended to CA use with grain at higher moisture content.

Currently, the gases, nitrogen or $CO_2$, required to create and maintain the atmospheres required for CA storage are supplied either as liquified gases in insulated tankers for large scale treatments or as compressed gas in cylinders or as dry ice for small scale application. We must ask whether these methods of supply are the ones of choice, or are better methods available, but just not used, and what alternatives appear feasible for use in the near future.

Supply of the gases by tanker or in cylinders is convenient. However, it must be difficult to justify economically the transport of gases, often over long distances, from some industrial production centre to the storage. This procedure requires expensive specialised vehicles or heavy cylinders and may contribute a significant part of the overall cost of CA use (e.g. see Banks and Annis, 1977; Connell and Johnston, 1981). However, the storage itself is surrounded both by inexhaustable supplies of nitrogen in the air and large quantities of carbon-containing material, agricultural wastes and even the grain itself, suitable for use as a $CO_2$ source. Methods of CA used in the future must surely include the generation of the required gases on site.

Research is already under way towards the replacement of the use of tanker gases and the development of on-site processes for gas supply for CA use. There have been successful full-scale field trials using atmospheres generated by burning hydrocarbons in air to provide a low oxygen gas mixture (e.g. Storey, 1973; Navarro *et al.*, 1979). There has been research on ways to improve the ancient and elegant technique of hermetic storage so that it can be used in above-ground structures (Burrell, 1980; Lu, in press). However, it is not widely realised how many different potential methods there are for the generation of the required gases. Some methods of production of nitrogen on site and their economics and scope of application were discussed by Zanon (1980). In this paper, I present a synopsis of the requirements a gas generation system must meet and then a survey of some possible methods[†]. The systems considered include both those producing pure nitrogen or $CO_2$ and also mixtures of these two gases. Data is given on the energy or fuel requirements of the processes. However these requirements will vary widely with storage capacity, and location and methods of energy accounting. Thus the values given must be taken as guides only. I hope that this speculative exposition may stimulate consideration of the various methods available and contribute towards the continued development of CA techniques as valuable tools for grain storage and protection.

## 2. SPECIFICATION FOR GAS SUPPLY FOR CA USE

In order to be able to judge the suitability of a particular gas production process, it is necessary first to have a specification for the basic parameters: the composition of the gas and its rate of supply. Unfortunately, neither of these are well defined even now, despite many decades of interest in CA techniques. The specifications are likely to change with experience and research in the future.

### 2.1 Composition

Research on the effects of various gas compositions (combinations of nitrogen, $CO_2$ and oxygen) on insects, microorganisms and the grain, has lagged behind the development of methods of applying these atmospheres in the field. We are now more certain of how to create and maintain a given composition than of the optimum atmosphere itself. There are several important problems yet to be resolved which may have a bearing on what is considered the optimum strategy in the future. In particular:

(i) It may be possible to use atmospheres containing several percent $O_2$ against insects if the exposure period is prolonged (e.g. several months).

(ii) The influence on insects of the $CO_2$ concentration in low oxygen atmospheres is not well understood or quantified.

(iii) There is little data on the effect on insects of long exposures at $< 35\%$ $CO_2$ in air.

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[†] Suppliers of equipment are given for example only. The equipment cited has not been tested by the author and there may be other suppliers of similar equipment which may or may not be more suitable for the purpose suggested.

(iv) There is insufficient data on quality effects and mould control to determine which gas mixtures are most suitable for use at > 60% equilibrium relative humidity.

(v) There is no data on whether a particular composition should be created slowly or rapidly for optimal insecticidal effect.

(vi) It has not been determined if $CO_2$ is detrimental to the structural strength of reinforced concrete storages by promoting the rusting of the reinforcing steel through carbonation of the concrete.

Against this uncertain background, the specifications given here (Table 1) for exposure periods and gas compositions cannot be taken as definite. Indeed two of the atmospheres discussed here are presented because I believe that similar atmospheres will be useful in the future. However, the scientific evidence on which this belief is based is indicative rather than conclusive.

## 2.2 Rate of supply

There are two separate phases in the use of CA techniques: an initial phase in which the desired atmosphere is created in the storage and a subsequent one in which the composition is maintained within set limits for the exposure period. These are referred to here as the 'purge' and 'maintenance' phase, following Banks and Annis (1977). The purge phase is taken here to include the creation of the desired atmosphere either by the direct addition of gas or by recirculation of the storage atmosphere through some device which modifies the composition appropriately (Fig. 1). The gas requirements for the two phases are summarised in Table 1.

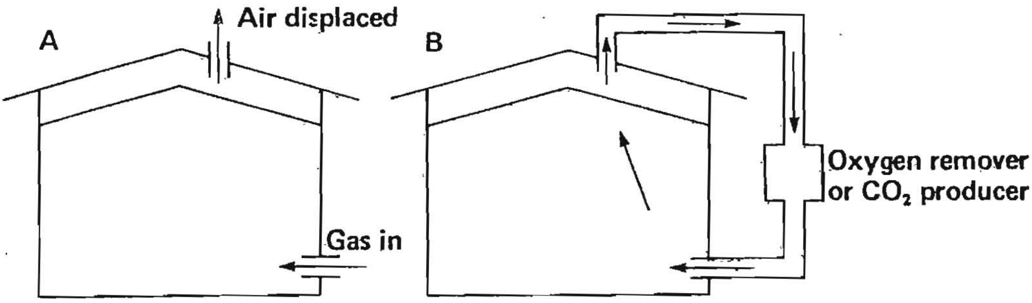


Fig. 1. Purge phase of the CA process. CA creation using a direct purge (A) or by recirculation (B).

TABLE 1.

Requirements for various controlled atmospheres, full storage in well sealed storages (pressure decay test time, > 5 mins, 500-250 Pa).

| Type of atmosphere | Target composition | Exposure period | Purge requirements | Maintenance requirements | Status of specification | Background References |
|---|---|---|---|---|---|---|
| Nitrogen-based atmosphere | $< 1\%\ O_2$ | > 24 days (25°C) | $1\text{-}2 m^3t^{-1}$ added very rapidly (< 1/2 day) | $0.01\text{-}0.06 m^3t^{-1}$ pure $N_2$ or remove $0.005\text{-}0.02 m^3t^{-1}d^{-1}\ O_2$ | Largely based on field experience with some laboratory data | Banks and Annis (1977) |
| Nitrogen-$CO_2$ mixture | $< 1\%\ O_2$ with $> 10\%\ CO_2$ | > 20 days (25°C) | $1\text{-}2 m^3t^{-1}$ added rapidly (< 2 days) | $0.02\text{-}0.12\ m^3\ t^{-1}\ d^{-1}$ of gas at $< 0.3\%\ O_2$ | Based on nitrogen specification with allowance for increased effect from $CO_2$ | Bailey and Banks (1980) |
| Hermetic storage atmosphere | $< 6\%\ O_2$ with $> 14\%\ CO_2$ | > 2 months | $0.1\text{-}0.3 m^3t^{-1}\ O_2$ to be removed over 10 days | $0.03\text{-}0.01 m^3t^{-1}\ d^{-1}\ O_2$ to be removed | Speculative | Spratt (1979 a,b) |
| High-$CO_2$ atmosphere | $> 70\%\ CO_2$ [a] in air | > 10 days | $0.5\text{-}1 m^3t^{-1}$ added rapidly (< 2 days) | None | Based largely on field experience | Banks (1979) |
| Intermediate-$CO_2$ atmosphere | $> 40\%\ CO_2$ in air | > 30 days | $0.3\text{-}0.5 m^3t^{-1}$ added over 10 days | $0.02\text{-}0.04 m^3t^{-1}\ d^{-1}$ pure $CO_2$ | Speculative | Stoyanova and Shikrenov (1976)<br>Lindgren and Vincent (1970) |

[a] Initial target composition. May decay to lower values during exposure period (see Banks, 1979).

The rates of gas supply for the purge and maintenance phases differ substantially. The ratio of these rates is typically between 10:1 and 100:1. At present the same gas supply process is used for both phases, but there is no reason why this should necessarily be so. Indeed, it may often be a better strategy to provide a system for purging, capable of high rates of gas output, that can be moved from site to site, and a much smaller system for the maintenance phase, dedicated to one site or storage unit only.

## 3. TECHNIQUES FOR GENERATION OF GASES FOR CA USE

The techniques for gas generation for CA use can be divided into three categories according to the gas mixture produced:

(i) Nitrogen producers (< 1% $O_2$).

(ii) Producers of a nitrogen-$CO_2$ mixture (< 1% $O_2$), including hermetic storage systems.

(iii) $CO_2$ producers.

The techniques available for production of these types of gas mixture are summarised in Tables 2, 3, and 4 respectively, together with comment on the scale of applicability, development status and energy or material consumed in course of supply of the gases. The energy and fuel requirements are calculated from a variety of sources, largely descriptive technical leaflets, and from data given by gas supply companies. No allowance is made for the energy cost of making the apparatus giving the gas. Hermetic storage systems are included in the category with producers of nitrogen-$CO_2$ mixtures, since similar principles of operation are involved. However, hermetic storage systems may not produce as low oxygen tensions as nitrogen-$CO_2$ producers (up to about 8% $O_2$ in some cases (see Banks, in press) compared with < 1% $O_2$).

Many systems are in use or obviously feasible but untried (e.g. pipeline supply). No detailed comment will be given here on these methods. The merits and principles of operation of the other systems are given below.

### 3.1 Potential systems for nitrogen production

3.1.1 *From exhaust from burning hydrocarbons in air.* Nitrogen can be extracted from the low oxygen exhaust stream produced by burning hydrocarbons in air (Zanon, 1980). $CO_2$, water and other impurities produced during combustion, can be removed by absorption from the gas stream on molecular sieve. A transportable plant producing 40 $m^3$

TABLE 2.

Techniques for producing or maintaining a nitrogen atmosphere (< 1% $O_2$).

| Technique | Phase best suited | Capital cost [a] | Scale of application best suited [b] | Development status | Primary energy or fuel requirement: Purge phase (per tonne grain) [c] | Primary energy or fuel requirement: Maintenance phase (per tonne grain per day) [d] |
|---|---|---|---|---|---|---|
| Liquified gas supplied by tanker and stored on site | Purge or maintenance | Very low | Intermediate to large | In use (Tranchino *et al.*, 1980; (Banks *et al.*, 1980) | 4.3 MJ + 0.4 mL diesel $km^{-1}$ [f] | 0.08 MJ + 0.0007 mL diesel $km^{-1}$ |
| Compressed gas supplied in cylinders | Purge or maintenance | Very low | Small | In use (Champ *et al.*, 1982) | 3.4 MJ + 0.24 mL diesel $km^{-1}$ | 0.06 MJ + 0.009 mL diesel $km^{-1}$ |
| Air separation on site (cryogenic) | Purge or maintenance | High | Very large | Feasible | 4.3 MJ | 0.08 MJ |
| Pipeline supply from cryogenic separation | Purge or maintenance | Low or intermediate | Intermediate to very large | Feasible | 3.3 MJ | 0.06 MJ |
| PSA | Purge or maintenance | Intermediate | Intermediate to large | Plant available | 1.8 MJ | 0.03 MJ |
| Nitrogen generation from hydrocarbon combustion | Purge | Intermediate | Intermediate to large | Plant available | 130 g $C_3H_8$ + 1.1 MJ | 2.5 g $C_3H_8$ + 0.02 MJ |
| Oxygen removed by hydrogen combustion [e] | Maintenance | Low | Small to Intermediate | Requires development | 0.3 $m^3$ $H_2$ | 0.004 $m^3$ $H_2$ |
| Catalytic oxidation of ammonia [e] | Maintenance | Low | Small to Intermediate | Requires Development | 120 g $NH_3$ | 1.6 g $NH_3$ |
| Direct electrolytic removal of oxygen [e] | Maintenance | Low | Small to Intermediate | Speculative | 4.7 MJ | 0.06 MJ |
| Chemical absorption of oxygen [e] | Maintenance | Very Low | Small | Speculative | Remove 6 g-mol $O_2$ | Remove 0.08 g-mol $O_2$ |

[a] Capital cost assessed as approximate cost to use on the following rating per site of 10,000 t: very low < \$5,000, low = \$5,000 - \$20,000, intermediate = \$20,000 - \$100,000, high > \$100,000.

[b] Rated according to the following approximate scale: small < 300 t, intermediate, = 300 - 10,000 t, large = 10,000 - 100,000 t, very large < 100,000 t. Allowance made for installation cost in assessment.

[c] Calculated for a filled 2,000 t capacity bin of total gas volume 1100 $m^3$, and headspace of 145 $m^3$ with 90% efficiency ($E_3$) of purging by direct introduction and 100% efficiency ($E_1$) by recirculation ($E_3$ and $E_1$ as Banks (1979)).

[d] Calculated for a filled 2,000 t capacity bin as *c* with input rate of 15 L $t^{-1}$ $d^{-1}$ for direct input, 7.5 L $t^{-1}$ $d^{-1}$ for recirculation.

[e] With recirculation.

[f] Transportation requirement based on 0.63 L diesel $km^{-1}$ for a 20 t gross load.

TABLE 3.

Techniques for producing or maintaining atmospheres of < 1% $O_2$ (< 2% for hermetic systems) with 10-20% $CO_2$, balance nitrogen

| Technique | Phase best suited | Capital cost [a] | Scale of application best suited [b] | Development status | Primary energy or fuel requirement: Purge phase (per tonne) [c] | Primary energy or fuel requirement: Maintenance phase (per tonne per day) [d] |
|---|---|---|---|---|---|---|
| Combustion of hydrocarbons from off-site sources ('open-flame') | Purge or maintenance | Intermediate | Intermediate | Demonstrated in field trials (Storey, 1973) | 66 g $C_3H_8$ + 0.03 MJ | 1.2 g $C_3H_8$ |
| Combustion of hydrocarbons from off-site sources [e] (catalytic) | Purge or maintenance | Intermediate | Intermediate | Demonstrated in field trials (Navarro *et al.*, 1979) | 47 g $C_3H_8$ + 0.15 MJ | 0.6 g $C_3H_8$ |
| Combustion of hydrocarbons from off-site sources (internal combustion engine) | Purge or maintenance | Low | Intermediate | Plant available but not tested in field (Banks, unpublished) | 66 g $C_3H_8$ | 1.2 g $C_3H_8$ |
| Liquified gases supplied by tanker | Purge | Very low | Intermediate to large | Feasible | 3.0 MJ + 0.03[f] mL diesel $km^{-1}$ | 0.08 MJ + 0.0008 mL diesel $km^{-1}$ |
| Compressed gases supplied in cylinders | Maintenance | Very low | Small | Feasible | 2.4 MJ + 0.17 mL diesel $km^{-1}$ | 0.06 MJ + 0.008 mL diesel $km^{-1}$ |
| Producer gas combustion | Purge or maintenance | Intermediate | Intermediate | Requires development | 66 g C | 1.6 g C |
| Biogas combustion | Maintenance | Intermediate | Intermediate | Requires development | 74 g $C_6H_{12}O_6$ | 1.4 g $C_6H_{12}O_6$ |
| Simple hermetic storage | Purge and maintenance | Very low | Small to intermediate | In use (Hyde *et al.*, 1973; Sigaut, 1980) | 150 g $C_6H_{12}O_6$ | 1.8 g $C_6H_{12}O_6$ |
| Assisted hermetic storage | Purge and maintenance | Very low | Small to intermediate | In use (Lu, in press) | 150 g $C_6H_{12}O_6$ | 1.8 g $C_6H_{12}O_6$ |
| Hermetic storage with sacrificed areas | Purge and maintenance | Very low | Small | Demonstrated in field trials (Burrell, 1980) | 150 g $C_6H_{12}O_6$ | 1.8 g $C_6H_{12}O_6$ |

[a] Capital cost assessed as approximate cost to use on the following rating per site of 10,000 t: very low < \$5,000, low = \$5,000 - \$20,000, intermediate = \$20,000 - \$100,000, high > \$100,000.

[b] Rated according to the following approximate scale: small < 300 t, intermediate, = 300 - 10,000 t, large = 10,000 - 100,000 t, very large < 100,000 t. Allowance made for installation cost in assessment.

[c] Calculated for a filled 2000 t capacity bin of total gas volume 1100 $m^3$, headspace 145 $m^3$, with a 90% efficiency of purging ($E_1$) by direct introduction and 100% efficiency ($E_1$) by recirculation ($E_1$ defined as in Banks (1979)).

[d] Calculated for a filled 2000 t capacity bin as *c* with input rate of 15 L $t^{-1}$ $d^{-1}$ for direct input, 7.5 L $t^{-1}$ $d^{-1}$ for recirculation.

[e] With recirculation.

[f] Transportation requirement based on 0.63 L diesel oil $km^{-1}$ for a 20 tonne gross load.

TABLE 4.

Techniques for producing or maintaining high- or intermediate-$CO_2$ atmospheres.

| Technique | Phase best suited | Capital cost [a] | Scale of application best suited [b] | Development status | Primary energy or fuel requirement | |
|---|---|---|---|---|---|---|
| | | | | | To make 70% $CO_2$ atmosphere (per tonne) [c] | To maintain 40% $CO_2$ atmosphere (per tonne per day) [a] |
| Liquified gas supplied by tanker and stored on site | Purge or maintenance | Very low | Intermediate to large | In use (Jay, 1971; Banks *et al.*, 1980) | 0.7 MJ + 0.03 [e] mL diesel $km^{-1}$ | 0.03 MJ + 0.0013 mL diesel $km^{-1}$ |
| Compressed gas supplied in cylinders | Purge or Maintenance | Very low | Small | In use (Champ *et al.*, 1982) | 0.7 MJ + 0.07 mL diesel $km^{-1}$ | 0.03 MJ + 0.003 mL diesel $km^{-1}$ |
| Pipeline supply | Purge or maintenance | Low to intermediate | Intermediate to very large | Being installed | 0.05 MJ | 0.002 MJ |
| Supplied as dry ice | Maintenance | very low | Small | In use (Sharp and Banks, 1980) | 1.8 MJ + 0.03 mL diesel $km^{-1}$ | 0.08 MJ + 0.0013 mL diesel $km^{-1}$ |
| Production on site from hydrocarbon combustion in oxygen | Purge or maintenance | Intermediate | Intermediate | Requires development | 300 g $C_3H_8$ or<br>610 g $C_6H_{12}O_6$ | 40 g $C_3H_8$ or<br>90 g $C_6H_{12}O_6$ |
| Production on site from carbon combustion in oxygen | Purge or maintenance | Intermediate | Intermediate | Requires development | 240 g C | 9 g C |
| Recovery from $CO_2$ containing gas streams | Maintenance | Intermediate | Intermediate | Plant available | varies with process | varies with process |
| Anerobic fermentation | Maintenance | Low or intermediate | Small to intermediate | Requires development | 610 g $C_6H_{12}O_6$ | 40 g $C_6H_{12}O_6$ |

[a] Capital cost assessed as approximate cost to use on the following rating per site of 10,000 t: very low < $5, low = $5,000 - $20,000, intermediate = $20,000 - $100,000, high > $100,000.

[b] Rated according to the following approximate scale: small < 300 t, intermediate, = 300 - 10,000 t, large = 10,000 - 100,000 t, very large < 100,000 t. Allowance made for installation cost in assessment.

[c] Calculated for a filled 2000 t capacity bin of total gas volume 1100 $m^3$ and headspace 145 $m^3$, with 80% efficiency of purging ($E_1$).

[d] Calculated for a filled 2000 t capacity bin as [c] with a gas interchange rate of 0.05 $day^{-1}$.

[e] Transportation requirement based on 0.63 L diesel oil $km^{-1}$ for a 20 tonne gross load.

$h^{-1}$ is available commercially (Kemp, Glen Burnie). The technique suffers from a high degree of mechanical complexity and has probably been superseded by the PSA system (see below).

3.1.2 *Pressure swing absorption.* The pressure swing absorption (PSA) system using air as feedstock. The process involves cycles of compression and decompression of the gas mixture in the presence of a carbon that possesses molecular sieve properties and relies on the difference in rate of absorption and desorption of nitrogen and oxygen in the carbon to achieve separation (Zanon, 1980). Nitrogen with < 0.3% residual oxygen can be conveniently produced by the process.

As in the case of nitrogen production from exhaust gases, the PSA systems are mechanically complex. Nevertheless both systems are capable of on-site use. Both produce gas more cheaply than from the usual cryogenic air separation system for nitrogen production (Zanon, 1980) and show promise as ways of obtaining nitrogen for CA use. There are several manufacturers of equipment apparently suitable for grain storage applications (e.g. Gastec, Salinas; Kemp, Glen Burnie; Techsep, London).

3.1.3 *Catalytic oxidation of ammonia.* The aerial oxidation of ammonia gas over a noble metal catalyst can be used to remove oxygen from air to give a low oxygen gas stream containing water according to the approximate equation.

$$\underset{\substack{\text{Ammonia}\\ \text{(1 vol)}}}{NH_3} + \underset{\text{air (3.6 vols)}}{0.75\ O_2 + 2.8\ N_2} \text{------>} \underset{\substack{\text{nitrogen}\\ \text{(3.2 vols)}}}{3.2\ N_2} + 1.5\ H_2O$$

The process has been proposed for producing atmospheres for CA storage of fruit (Anon., 1971). Figures for minimum oxygen levels produced are not available but could be very low. For use with grain, the process would need development to ensure that no nitrogen oxides or residual ammonia were added to the storage and the water was removed.

This process appears worthy of close consideration as a method of maintenance for nitrogen atmospheres. Anhydrous ammonia for use as a fertilizer is available in many grain growing regions. It is easily stored with low toxicity and flammability risks. However, the production of ammonia requires substantial energy input. Transport costs may also be important.

3.1.4 *Hydrogen combustion* Combustion of hydrogen in air removes oxygen with the formulation of water according to the approximate equation:

$$\underset{\substack{\text{Hydrogen}\\(1\ \text{vol})}}{H_2} + \underset{\substack{\text{air}\\(2.4\ \text{vols})}}{0.5\ O_2 + 1.9\ N_2} \dashrightarrow \underset{\substack{\text{nitrogen}\\(1.9\ \text{vols})}}{1.9\ N_2} + H_2O$$

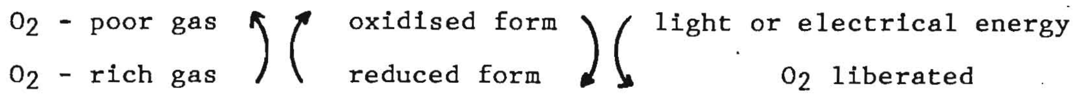
The process can be carried out in a direct combustion system or, more conveniently, over a catalyst. Industrially-produced hydrogen supplied in cylinders could be used for removing oxygen from an atmosphere by recirculation through a combustion system. However transport costs for the heavy and bulky cylinders containing the hydrogen would probably rule this out. However, hydrogen does appear potentially useful as a fuel for removing oxygen during the maintenance phase, where much lesser quantities are required. Combustion of hydrogen and oxygen can be achieved at normal ambient temperature over some catalysts, a substantial advantage over catalysts for propane combustion which require heating to more than 300°C before they operate efficiently. The hydrogen could also be produced by electrolysis of water on site or perhaps by photolysis of water with sunlight, a system currently under active research (Wrighton, 1983; Anon., 1982). It would be necessary to remove the water produced during combustion.

Catalytic oxidation of hydrogen (e.g. with a Deoxo unit (Engelhard Industries, Newark)) could also be used to further lower the oxygen content of a low oxygen stream (e.g. 0.5%) produced by another process. This option is already available for PSA systems (e.g., with Techsep systems (British Oxygen Co., London.))

3.1.5 *Direct electrolytic or photolytic removal of oxygen.* Various inorganic ions can be reversibly reduced and reoxidised, with liberation of oxygen during the electrolytic reduction and subsequent direct reoxidation of the species by molecular oxygen. For instance:

$$Cr^{+++} + \epsilon \underset{-O_2}{\overset{+O_2}{\leftrightarrows}} Cr^{++}.$$

It may be possible to find materials (e.g. cobalt-organic complexes similar to those discussed in McLendon and Martell (1976)) which can reversibly bind oxygen in the dark and liberate it in light. These reversible reactions could be used to remove oxygen from a gas stream:



The direct current electrical energy required could be supplied from a photovoltaic device (solar cell), where the light could be sunlight itself.

This scheme is still only speculative but there is much research interest in similar fields for the photolytic generation of hydrogen (Wrighton, 1983; Anon., 1982). Because of its lack of moving parts or dependence on external material or energy supplies, the scheme appears to merit investigation.

3.1.6 *Removal of oxygen by chemical reaction.* It may be possible to develop oxygen-removal processes based on materials which react reversibly with oxygen, perhaps chemically similar to the biological oxygen carriers (e.g. systems described by Basolo, 1978). In small scale CA applications, a reactive material could be provided in a recirculation system with sufficient capacity to absorb all the oxygen leaking into the system during the exposure period.

### 3.2 Potential systems for nitrogen-$CO_2$ mixtures

3.2.1 *Combustion of hydrocarbons from off-site sources.* There are machines available which produce gases for CA storage of fruit by burning hydrocarbons in air to remove oxygen. Because the fruit, such as apples, generally cannot tolerate $< 2\%$ $O_2$ and more than a little $CO_2$, these machines are not directly suitable for use for CA storage of grain. In general they could be adapted, with suitable tuning, to give a lower oxygen level and remove the water formed.

The combustion of propane in air follows the equation

$$\begin{array}{llll} C_3H_8 \; + & 5.0\ O_2 + 18.8\ N_2 & \text{---->} & 3.0\ CO_2 + 18.8\ N_2 + 4\ H_2O \\ \text{propane} & \text{air} & & 14\%\ CO_2,\ 86\%\ N_2 \\ \text{(1 vol)} & \text{(23.8 vols)} & & \text{(21.8 vols)} \end{array}$$

There are three forms of burner:

(i) 'Open flame' burners (e.g., those from Capco, Melbourne and Gas Atmospheres, Port Washington (Anon., 1981)).

(ii) Catalytic burners (e.g. Arcat and Tectrol systems).

(iii) Internal combustion systems.

In open flame burners, air and propane are burnt continuously in a combustion chamber. They are capable of producing high rates of gas at low oxygen tension. Catalytic systems can be used in a recirculation system. They do not give as high rates of gas output and only reduce the oxygen concentration by a fixed fraction (e.g. to one third) during passage through the catalyst. Catalytic systems use less propane per tonne grain stored than open flame to create a low oxygen environment. However, they consume more electrical power, particularly in the later stages of the oxygen removal where heat is required for the catalyst to maintain the catalyst at a high temperature (see Table 3). Presumably open flame systems can be modified with suitable mixture control to allow combustion of the propane in a mixture of fresh air with some recirculated gases, thus reducing the oxygen concentration in the combustion mixture and thereby using less fuel.

The third alternative, a modified internal combustion engine, is currently under development at CSIRO Division of Entomology (Wiseman and Banks, 1979). Its main advantage over the other systems is that it can be easily made independent of cooling water and electricity requirements that can often pose a problem in arid or remote, unserviced areas. Also the output flow can be regulated over a wide range, giving a system which may be suitable for both purging and subsequently maintaining a storage under a low oxygen atmosphere.

3.2.2 *Producer gas combustion.* A variety of carbonaceous materials, including wood, straw, rice hulls and other agricultural wastes, can be converted by combustion in a limited supply of air to producer gas; a gas mixture of variable composition depending on the fuel, but typically about 30% $CO_2$ with the balance largely inert gases. Producer gas could be burnt with air to give a low oxygen exhaust mixture in systems such as given in Section 3.2.1. A typical combustion equation using producer gas from charcoal (Breag and Chittenden, 1979) would be:

$$\underbrace{0.3\ CO + 0.04\ H_2 + 0.04\ CO_2 + 0.62\ N_2}_{\text{producer gas (1 vol)}} + \underbrace{0.17\ O_2 + 0.64\ N_2}_{\text{air (0.8 vol)}} \longrightarrow$$

$$0.34\ CO_2 + 1.26\ N_2 + 0.02\ H_2O$$

$$21\ \%\ CO_2,\ 79\%\ N_2\ (1.6\ \text{vols})$$

Producer gas systems, using coke, have been used for generating CA gases for grain storage in the past (Winterbottom, 1922), though the purity of the gas used then would not meet today's standards (e.g. CO often > 5%, U.S. maximum permitted level 4.5% (Anon., 1980)).

A producer-gas-based system has two important advantages over propane-based ones: it can use locally produced and easily stored fuels and, with charcoal as fuel, very little water is produced during combustion. Water removal from the combustion gases in propane-based burner systems makes the apparatus required much more complex. Note, however, that propane-fuelled systems give about 1.5x as much gas per mole of carbon burnt as given by producer gas systems.

3.2.3 *Combustion of methane from fermentation.* Many agricultural wastes (e.g. straw) can be fermented anaerobically to produce a methane-rich gas called biogas, typically 50% $CH_4$, 50% $CO_2$ when produced from carbohydrates (Lane, 1980, 1981). Combustion of biogas in a burner as described in Section 3.2.1. would give a low oxygen gas suitable for CA use. Biogas combustion in air typically follows the equation:

$$\underbrace{0.5\ CO_2 + 0.5\ CH_4}_{\text{Biogas (1 vol)}} + \underbrace{1.5\ O_2 + 5.6\ N_2}_{\text{air (7.1 vols)}} \longrightarrow \underbrace{1.0\ CO_2 + 5.6\ N_2}_{\substack{15\%\ CO_2,\ 85\%\ N_2 \\ (6.6\ \text{vols})}} + 2.0\ H_2O$$

Biogas must be generated in a specially constructed digester. Gas storage facilities may be required to cope with changes in output and usage rates. Both items may result in significant capital cost on site. Waste heat from biogas combustion could be used to maintain the fermentation at optimum temperature. Biogas systems produce slightly less gas, about 0.9x per mole of carbon burnt, than propane-fuelled systems. Biogas sytems appear very suitable for CA generation in less developed regions because locally produced fuels are used, methods of constructing digesters have been developed relying only on local materials (Lane, 1981; Meynell, 1982) and there is no need for extensive mechanical servicing and parts required by more complex systems.

3.2.4 *Hermetic storage with sacrificial areas.* Storages must be very well sealed and permit very low gas interchange rates with the external atmosphere, if they are to be suitable for true hermetic storage of dry grain (< 12% m.c.) (Oxley *et al.*, 1960). Even with grain of 12-16% m.c., the rate of air ingress must be very low to ensure that mould and insect growth is restricted. In order to create low oxygen tensions in more leaky structures, it is necessary to increase the rate of respiration within the structure so that initial insect infestation cannot persist (e.g. as observed by Oxley and Wickenden, 1963). This may be accomplished either by seeding a small region of the stored commodity with a large number of insects (S.W. Bailey, unpublished data) or by intentionally wetting a small region of the bulk (Burrell, 1980) thus stimulating mould growth and respiration. In either case it is useful to provide some form of gas permeable containment of the sacrificial region so that it can be removed and discarded when the commodity is removed.

3.2.5 *Assisted hermetic storage.* The category 'assisted hermetic storage' is used here to define a hermetic storage process, with the reduction of oxygen level, occurring normally by respiration activity in simple hermetic storage, augmented by some other controlled process, usually external to the storage system. It is distinguished from 'sacrificial' storage by the higher degree of control of the oxygen removal process. In sacrificial storage there is no regulation of the rate of oxygen removal after the initiation of the process. An elegant example of assisted hermetic storage is now in use in China (Lu, in press). In this case to remove oxygen the storage gases are circulated through an enclosure containing racks of moist grain and bran seeded with a particular mould culture.

### 3.3 Production of gas for high- and intermediate-$CO_2$ atmospheres

3.3.1 *On-site production by burning carbon-containing materials in air.* $CO_2$ can be collected from a gas stream by reversible sorption processes (e.g. into ethanolamine, with the Vetrocoke process or by PSA systems). Such a process could be used to remove $CO_2$ from the exhaust from the burning of hydrocarbons in air, to give a $CO_2$-rich gas at an adequate concentration (> 70% $CO_2$) for creation or maintenance of a high- or intermediate-$CO_2$ atmosphere. Small-scale industrial plant operating on this principle and utilizing fuel oil as a $CO_2$-source is available. Presumably the process could be used to recover $CO_2$ from gas streams from fermentation processes or from burning producer gas or biogas.

3.3.2 *On-site production from burning coal or charcoal in oxygen.* Burning carbon directly in oxygen could produce pure $CO_2$ directly. The easily available carbon sources, dried powered coal, coke and charcoal, all contain sufficient residual hydrogen compounds to produce some water during combustion and would produce a gas requiring purification to remove undesirable contaminants such as sulphur-containing material or unburnt hydrocarbons. Nevertheless this system appears to be a possible route to producing a $CO_2$-rich gas

(> 70%) without the need for extensive drying or enrichment of the combustion products.

Oxygen of adequate purity could be supplied on site by a PSA system or on a smaller scale by direct photolysis or electrolysis of water or from plant photosynthesis.

3.3.3 *$CO_2$ from fermentation.* $CO_2$ is produced industrially from the anerobic fermentation of carbohydrates by yeasts and other organisms. Presumably $CO_2$ could be produced close to a grain storage, providing a source of gas for CA use and fermentation products (ethanol, industrial solvents, etc.) at the same time. By carrying out fermentation near grain production regions, the energy cost of the transport of grain to processing centres is avoided and products valuable to the food grain storage system are made locally. Low quality or high moisture grain could be used as a feedstock. Other carbohydrate-containing material, notably straw, can also be used.

## 4. DISCUSSION

With such a wide range of possible processes for the creation of suitable atmospheres for CA storage it is difficult to make a choice as to which may be dominant in the future. The situation is further complicated by the inadequacy of our knowledge on what is the optimum gas composition for particular situations. Nevertheless there are some generalisations and predictions which can be made reasonably:

(i) CA systems will be generated by means other than from tanker-delivered gases. This is particularly relevant to sites distant from industrial centres.

(ii) The greater fuel consumption of on-site $CO_2$ generation processes place these systems at a disadvantage relative to the processes giving nitrogen/ $CO_2$ mixtures.

(iii) Unless $CO_2$ is found to be detrimental (e.g to quality or structures), processes giving mixtures of nitrogen and $CO_2$ with low oxygen contents are the most likely to be used for CA grain storage at sites distant from industrial centres in the future since their energy requirements are low.

(iv) Systems of CA generation will incorporate some recirculation to permit the refining of some of the internal gas so that its composition remains within specification.

(v) Simple, passive systems of CA generation will be developed which may find widespread application, displacing those systems relying on much machinery (e.g. burners, PSA systems).

(vi) CA generation systems will be developed which utilize materials available cheaply, close to the site of use. These will include agricultural wastes and air.

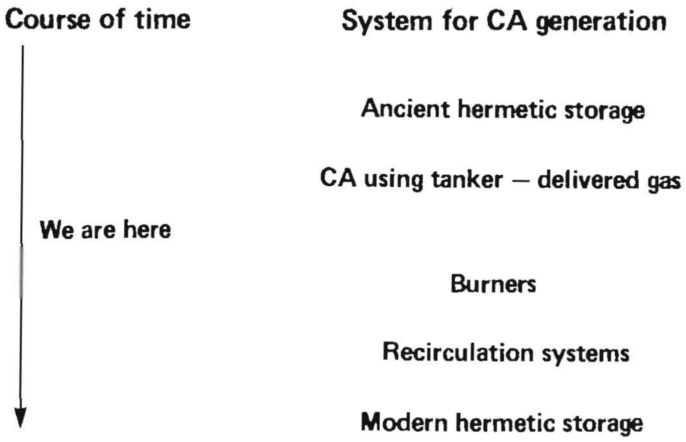


Fig. 2. Time chart for the progress of methodology for CA generation for grain storage.

In the spirit of these comments, I predict a progression in the processes used for CA generation as given in Fig. 2. The ancient hermetic storage system has been in use, almost unchanged, for several thousand years. Tanker gas-based systems and their forerunners using dry ice or cylinders have been available for a few decades. Burner systems have been used but are still largely in the research phase of development. Recirculation systems for CA use have been demonstrated but are not yet in routine use. Lastly, we reach the system I term 'modern hermetic storage', where the elegant process of hermetic storage is refined and controlled so that it meets the current constraints of grain handling and marketing, utilizing a small, and perhaps substandard, portion of a commodity stock, as a source of gas, to preserve the remainder. The current interest and speed of development of systems in CA grain technology suggest that we could reach Time Level 5 by 2000 AD.

There is no reason why any of these processes should become the sole system for CA generation. Indeed it is likely that all will exist together in time, with the use of particular systems dictated by local conditions. In some places, grain storage may develop so that some of the products of the system used for CA generation (e.g. fermentation products) may become industrially useful, contributing to the economics of the storage process. In other places, simple solutions may be more appropriate.

It can be seen that much remains to be done before CA technology can be regarded as fully developed. Nevertheless enough is now known at least for the problems to be defined. Let us hope that they are now solved quickly so that CA systems will continue to play a prominant and well founded role in grain storage.

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