CONTROLLED ATMOSPHERE STORAGE OF GRAIN: THE KNOWN AND THE FUTURE

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Abstract

Controlled atmosphere (CA) storage techniques for disinfestation of grain have been available fully developed for almost two decades. Detailed procedures have been published for large permanent grain stores, sheeted bag-stacks, shipping containers and small-scale packaging. This paper outlines the information on CA storage of grain, summarising data on exposures required to control insects, effects on microorganisms and the commodity, and technical aspects of gas application.

CA techniques have an important role in integrated systems for protection of grain, with particular application where residue-free, *in situ* treatments are needed. With the increasing restrictions being placed on chemical treatments of grain, CA techniques are likely to be used much more widely in the near future.

A major constraint on use of CA has been the cost of gas, hitherto usually delivered from off-site sources in liquid or compressed form. Recent developments of on-site generation systems for gases suitable for CA, hydrocarbon burners, membrane separation and PSA systems, make the technique more versatile and commercially attractive. Current substantial capital costs of generators are likely to fall as CA use increases, favouring still wider application of the technique.

1. INTRODUCTION

Controlled atmosphere (CA) techniques for storage of dry grain are not yet widely accepted. However the technology is well developed and, if the physical resources were available, could be applied immediately in most storage situations. The general requirements for CA storage of grain have been known since the mid-1970's. The three principal types of atmosphere, N_2-based, CO_2-based and burner gas systems (Table 1), were all demonstrated then (Shejbal 1980). The gas and structural (storage) requirements were defined and the action of various CA on target organisms, insect pests and moulds, were known in sufficient detail to define exposure periods reasonably accurately. There has been some progress in the technology since then, but this has been in the nature of minor refinements or application to new situations rather than radical change. In this paper we set out to review the current state of knowledge on CA application and speculate on the future use of CA in grain storage.

TABLE 1: CA FOR GRAIN STORAGE

Atmosphere	Typical Composition
High-CO_2	60% CO_2, balance air
Low-O_2	1% O_2, balance N_2 and inerts
Burner gas	1% O_2, 12% CO_2, bal. N_2 and inerts

There appears to be a resurgence of interest in CA techniques for grain disinfestation though, as yet, this has been more towards theory rather than practice. Clearly one of the driving forces is the increasing difficulties and restrictions that now confront the more chemically based pest control measures: fumigation and control with protectants. Increasingly, sophisticated markets are expecting that grain should be 'residue-free' or contain much lower levels of residues resulting from pest control than hitherto acceptable. Legislative restrictions, reflecting concerns over the environment and worker safety, are making fumigation much more complex and costly to carry out and, in some cases, effectively prevent use of this technique. In addition there are also pressures from costs, and development of tolerance by insect pests to chemical treatment measures.

It is not surprising therefore that attention is being turned towards CA systems. There are very few well developed alternatives to chemically-based disinfestation for stored grain that can, alone, meet the requirement that grain be insect-free at point of sale or export. These are:

- CA techniques
- Heat disinfestation
- Low temperature storage
- Radiation disinfestation

What is surprising is that there seems to be so little preparation for change. Each of these options will require modification of plant and operating procedures with substantial lead times and financing needs. CA techniques are the only one of these options that can treat grain *in situ*. They will require well sealed stores and reliable cheap supplies of gas. Sealing technology and gas supply needs are summarised here, reinforcing the view that change-over from one pest control system to another cannot be instantaneous. Planning for a change to CA will have to start now if the technique is to be widely implemented soon.

There are a number of reviews and other publications on aspects of CA technology which set out most of the material, summarised below, in more detail. These concern the effects of CA on insect pests (Annis 1987, Bailey and Banks 1980), and microorganisms (Hocking 1990), the application of CA to silo bins (Banks and Annis 1977, Jay 1980, Ripp et al. 1984) and stacks of bagged produce (see Champ et al. 1990), technology of sealing of storages (Newman 1990), supply of CA gases (Banks 1984) and effect of CAs on commodity quality (Banks 1981, Gras and Bason 1990).

Almost all commercial installations currently using CA for grain utilise CO_2 atmospheres. These have several operational advantages over the alternative low-oxygen systems. Notably they can be used with 'one-shot' application, where no additional gas is required to maintain the atmosphere, provided a high concentration is achieved initially, typically >70% CO_2, and the seal of the storage restricts the gas loss to less than 0.05 d^{-1}. With low oxygen systems it is almost inevitable that the atmospheres will need to be maintained in some way. The rate of gain of oxygen by leakage is almost always too great to permit an acceptable atmosphere to be maintained for a sufficient time without it. Table 2 shows the loss rates we have observed from well sealed systems and an estimate of the time taken for the average concentration to rise above 2% from 1% O_2, a typical target concentration for insecticidal action. Bailey (1955) suggested 2% oxygen as the upper limit for effective CA. Despite problems with low-oxygen CA for grain there have been some recent developments which should make it of interest again. These are the development of burners and nitrogen generators, both offering low cost on-site generation of low-oxygen CA. These machines are discussed further below.

TABLE 2: TYPICAL GAS LOSS RATES FROM WELL SEALED STRUCTURES UNDER AUSTRALIAN CONDITIONS. BANKS AND ANNIS, UNPUBLISHED DATA.

Storage Type	Loss rate (d^{-1})	Days taken to change concentration at this loss rate	
		Initial - Final $1\% O_2$ - $2\% O_2$	Initial - Final $70\% O_2$ - $35\% CO_2$
Silo bins	0.02	2.6	35
Sheds	0.04	1.3	17
Bunkers	0.03	1.7	23
Bag stacks	0.01	5.1	69
Farm bins	0.05	1.0	14

2. THE BASIS OF CA STORAGE OF GRAINS

2.1 EFFECT ON INSECT PESTS

Annis(1987) has given an exposure schedule for application of nitrogen and CO_2-based controlled atmospheres to grain storages that, on the basis of current knowledge, will eliminate all grain storage pests, with the exception of *Trogoderma* species as diapausing larvae. This schedule is modified here (Table 3) to include the effects of burner gas atmospheres, typically containing <1% O_2, about 12% CO_2 with balance nitrogen and inert gases. There is some scope for reduction in exposure times in circumstances where only known susceptible species are present (e.g. in dried fruit or oilseeds in Australia where the tolerant *Rhyzopertha* and *Sitophilus* species will be absent).

TABLE 3: EXPOSURE SCHEDULE FOR CA FOR INSECT CONTROL IN GRAIN. COMMODITY TEMPERATURE 25-29°C. MODIFIED FROM ANNIS (1987).

Atmosphere	Composition	Exposure (days)
High-CO_2	70% initially, >35% at end	15
Low-O_2	1% O_2, continuously	21
Burner gas	1% O_2, continuously	14

Temperature has an important effect on exposure times needed to kill grain pests and allowance has to be made for this in dosage recommendations. Fig. 1 shows the influence of temperature on kill of *Sitophilus oryzae* adults for both low-oxygen and high-CO_2 atmospheres, indicating a steep but similar effect. Similar effects are presumed for other stages and species. At high commodity temperatures, (>30°C), that often prevail at harvest in many countries, CA can provide a rapid means of disinfestation, with exposures of 7-10 days. Conversely, in colder regions, exposures of more than one month may be needed to achieve a complete kill.

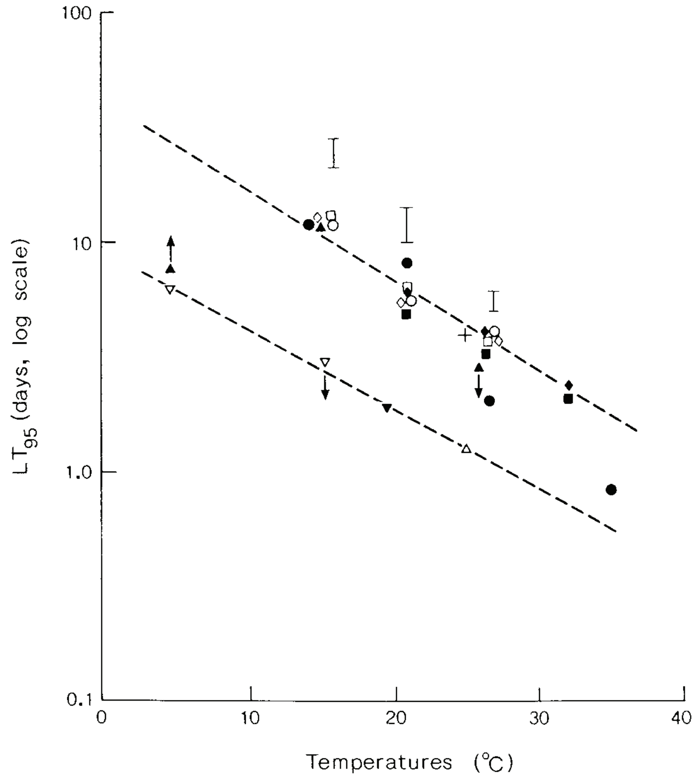

FIGURE 1. Temperature sensitivity of *Sitophilus oryzae* adults in: low-O_2 atmospheres (upper line) ●, burner gas, <1% O_2 and 9% CO_2, ◊, 100% He, □, 100% N_2, O, 100% CO_2, ▲, <1% O_2 , ■, ~0.5% O_2 , ♦, ~1.0% O_2, +, 100% CO_2) and high-CO_2 concentrations in air (lower line) (∇, 60%, ▼, 75%, Δ, 65%). Arrows indicate direction of uncertainty in data points; bars show exposure periods recommended by Jay (1980) for high-CO_2 atmospheres at various temperatures. Figure from Banks and Annis (1990).

From the limited data available (Table 4) it is preferable to use high-CO_2 atmospheres against beetle pests classed as 'internal feeders' and against moths, but to use low-oxygen atmospheres against beetle pests that feed externally (i.e. those that do not develop within the grain kernel) when as brief an exposure as possible is required for disinfestation.

In general there has been sufficient research into high-CO_2 and low O_2 atmospheres to be confident of the schedules given in Table 3. However, more information is needed for:

- nitrogen-based atmospheres containing more than 2% O_2,
- and CO_2-based containing less than 35% CO_2

These will certainly require long exposure periods for full effectiveness, but may be more economical than those in Table 3 as they will be easier to create and maintain.

TABLE 4: RELATIVE SUSCEPTIBILITY OF INTERNAL AND EXTERNAL FEEDERS TO HIGH-CO_2 AND LOW-O_2 ATMOSPHERES (Banks and Annis 1990).

Species	Stage*	Type of feeder	Atmospheres compared: Quicker acting	Atmospheres compared: Slower acting
Rhyzopertha dominica	E, L, P, A	Internal	60% CO_2 in air	99% CO_2, 0.2% O_2
Sitophilus oryzae	E, L, P, A	Internal	60% CO_2 in air	99% N_2, 1.0% O_2
Sitophilus zeamais	E, L, P	Internal	60% CO_2 in air	99% CO_2, 0.2% O_2
Ephestia cautella	E, L	External	99% N_2, 1.0% O_2	63% CO_2 in air
Ephestia cautella	P	External	63% CO_2 in air	99% N_2, 1.0% O_2
Tribolium castaneum	E	External	63% CO_2 in air	99% N_2, 1.0% O_2
Tribolium castaneum	L, P, A	External	99% N_2, 1.0% O_2	63% CO_2 in air
Trogoderma glabrum	L, L(d), P	External	99% CO_2, 0.2% O_2	61% CO_2 in air
Trogoderma variabile	L, P	External	99% CO_2, 0.2% O_2	61% CO_2 in air
Oryzaephilus surinamensis	L, P, A	External	98% CO_2, 0.4% O_2	62% CO_2 in air

* E, eggs; L, larvae; (d), diapause; P, pupae; A, adults.

2.2 EFFECT ON MICROORGANISMS

There is limited scope for use of CA, similar to those used against insect pests, for regulation of mould development. Many microorganisms important to grain storage are inhibited only slightly or not at all by CA. These include yeasts, *Lactobacillus* and some hydrophilic moulds. However it appears at least with low-oxygen atmospheres that there is a correlation between sensitivity to CA and ability to multiply at lower water activities. Table 5 summarises this trend. CA may thus be able to extend storage life of grains at moisture normally considered marginal for safe storage (i.e. a_W= 0.7 to 0.8).

TABLE 5: RELATIVE TOLERANCE OF STORAGE MICROFLORA TO LOW-OXYGEN ATMOSPHERES. ADAPTED FROM RICHARD MOLARD et al. (1987)

Microorganism	a_W	Equivalent wheat moisture content	Tolerance
Lactic bacteria Most yeasts	0.90	20	High
Field fungi	0.85	18	Medium
Some xerophilic yeasts	0.80	17	Medium
Xerotolerant storage fungi	0.75	16	Low
Xerophilic storage fungi	0.70	14	Low

The successful full scale trials by the Assoreni group (Shejbal 1980) using nitrogen-based atmospheres and subsequent limited commercial adoption were carried out under these conditions. They showed substantial control of moulding. It is unfortunate that CA do not kill, but only inhibit growth of most spoilage fungi, so when used for mould control they have to be maintained throughout the storage period. Unless adequate precautions (drying) are taken when such commodities are removed from the CA, the moulds multiply rapidly, providing adequate moisture is present and the commodity is warm.

2.3 EFFECT ON THE COMMODITY

In general no significant adverse effects have been noted on dry commodities (a_W<0.65) stored in CA at normal storage temperatures (<30°C). There is some evidence (Gras and Bason 1990) that high-CO_2 atmospheres at high temperatures (60°C) are slightly detrimental to retention of germination and may increase dough development times for flours from treated wheat. There may be some adverse effect on retention of viability in maize and barley under very low oxygen atmospheres (0.2% O_2). Overall the detrimental effects of CA, if any, are minor compared with that caused by small changes in moisture and temperature and are unlikely to be commercially significant.

3. TECHNICAL SPECIFICATIONS FOR CA USE

The technical requirements for CA use refer to:

- the modification of the storage structure to accept and retain added gas, and
- how and at what rate the gases are supplied.

3.1 MODIFICATION OF THE STORAGE - SEALING

There is a balance between the rate of degradation of a CA by leakage and the rate gas can be supplied economically to maintain it. This balance influences the cost and effort that can be put into sealing the store. Until recently the cost of the gas was significant, usually greater than \$A0.30m^{-3}, and it was necessary for the treated enclosure to have a high standard of sealing so that gas use was minimised. Both theoretical considerations and practical experience led to a single specification as the minimum likely to be acceptable. This level of sealing was defined as that which gives a pressure half-life of greater than 5 minutes when the structure was full (for further discussion of this test see Banks and Annis 1984). There is some evidence (Wilson et al. 1984) that if a 15 minute pressure half-life is attainable easily this is advantageous, as it further restricts gas loss. Recent development of lower cost gas sources may make it economical to relax the standard with increased gas consumption offset by cheaper supplies. However, provision of a verifiable standard for appropriateness of a CA application in a structure is crucial to the reputation of the process. A system requiring 'add a bit more if it does not work the first time' is difficult to market and use. The basic physics of gas loss from enclosures precludes reliable CA in poorly sealed storages except at intolerably high gas usage rates.

Reaching appropriate levels of sealing is clearly no technical impediment to CA use, although there appears to be reluctance to believe that it can be achieved economically. Existing large sheds (capacity >10,000t), concrete cells (~ 2000t capacity) and farm silo bins, (typically 50t capacity), are all routinely sealed in parts of Australia and the necessary sealant technology is well developed. PVC enclosures over bag stacks of grain can be made reliably to this standard. The types of structures that have been routinely sealed or built sealed to a 5 minute pressure standard and indicative costs of retrosealing existing structures in Australia are shown in Table 6 and 7 respectively.

TABLE 6: STRUCTURES ROUTINELY SEALABLE TO MEET A 5 MINUTE PRESSURE HALF-LIFE STANDARD

Silo bins (concrete and metal)

Farm bins (metal)

PVC-covered bunkers

Bag stacks

Large sheds (metal roof, concrete or metal walls)

TABLE 7: INDICATIVE COSTS FOR ROUTINE SEALING TYPICAL UNSEALED STORES IN AUSTRALIA

Storage Type	Capacity (t)	$A per tonne
Large sheds	25,000	3-7
Capped concrete cells	2,000	8-15
Bag stacks	200	7-10
Farm bins	50	14-25

3.2 DISTRIBUTION OF DUCT WORK

Storages require very simple modification to accept CA gases. In general no internal ductwork is required in cells to accept either nitrogen or CO_2 but some form of inlet, shielded to prevent clogging by grain, must be provided. In tall structures, CO_2 atmospheres must be recirculated at about one volume change per day via an external duct to prevent low concentrations developing in the upper parts of the structure. Distribution ductwork (similar to aeration ducts) is advantageous for rapid removal of the CA.

3.3 SUPPLY OF GAS

So far all published accounts of CA treatments of large grain bulks have described the use of atmospheres created either from industrially-produced gases, nitrogen or CO_2, delivered in pure form or by on-site controlled burning of hydrocarbons in air. Both systems have been demonstrated as feasible in a wide variety of structures, and are summarised in Table 8.

TABLE 8: STORAGE TYPES IN WHICH SUCCESSFUL CA GRAIN DISINFESTATION TREATMENTS HAVE BEEN CARRIED OUT

		Atmosphere		
Storage type	**Capacity (t)**	**High-CO_2**	**Low O_2**	**Burner**
Large sheds	25,000	C	*	*
Large silo bins	2,000	C	C	C
Farm bins	50	C	E	*
Bag stacks	200	C	E	*
Containers	18	C	*	*
Retail packs	0.001	C	C	*

C = In commercial use, E = Demonstrated in trials, * = No data available

The efficiency of purging of a store to create the atmosphere initially has been quite high, despite rudimentary distribution systems. Typical usage values in well filled, sealed structures are given for various gas sources in Table 9.

TABLE 9: TYPICAL GAS REQUIREMENTS TO CREATE CA IN FILLED, WELL SEALED WHEAT STORAGES

Atmosphere	Application rate to give target composition
High-CO_2	1-2 tonnes per 1000t
Low-O_2	1-3 m^3 per tonne
Burner gas	0.08 - 0.3 kg propane per tonne

Note: lower estimate refers to full 2000t silo bins.

Once created the atmosphere requires further input of gas to maintain its composition, if it is a low oxygen type; but usually does not, if high-CO_2 atmospheres are used.

3.3.1 Change away from CO_2

The recent development of the PSA (Pressure-swing Absorption) and membrane separation techniques for extracting N_2 from air have much potential to change the economics and feasibility of CA based on low oxygen atmospheres. Both are now used as sources of nitrogen for CA preservation of quality of fresh fruit stored in structures of similar size to large grain stores. They are yet to be tested thoroughly for grain, for which somewhat lower oxygen concentrations are needed when rapid disinfestation is required. Typically CA storage of fruit, such as apples, requires 2% O_2 whereas <1% is usually needed for grain. The choice storage of the appropriate system will depend largely on economics, since the output, nitrogen with a specified oxygen content, is the same for each machine. Projected running costs are given in Table 10 for various storage situations. Pure nitrogen, as liquid or compressed gas supplied from off-site sources remains an alternative and has the advantage of low capital requirements for the user and a guarantee of supply at very low (<0.39%) oxygen content.

Fig. 2 shows the combinations of supply rate and nitrogen purity where particular systems are most economic under U.S. conditions (low transportation, energy and interest costs) with the shaded area denoting recent advances in membrane separation technology. It will be seen from Fig. 2 that for small use (less than $10m^3h^{-1}$ and at $<1.0\%O_2$) membranes and cylinder supply are most suitable. This is in the range of the typical small farm bin (50t, $65m^3$). For very large requirements e.g. $1000m^3h^{-1}$, such as could be needed for rapid purging of a 25,000t storage, liquid supply appears most appropriate, with the capital cost of the equivalent on-site system, PSA, is likely to be prohibitive.

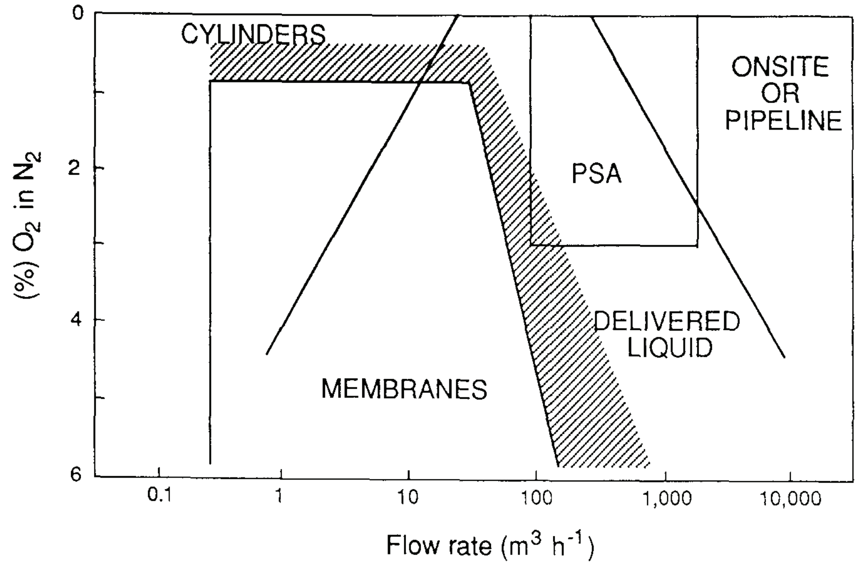

FIGURE 2. Combination of supply purity and flow rate where particular methods of nitrogen supply are most efficient. Shaded area represents recent advances in membrane technology. Modified from Spillman (1989).

TABLE 10: APPROXIMATE CAPITAL AND RUNNING COSTS FOR SUPPLY OF NITROGEN OR BURNER GAS (0.8% O_2) FOR VARIOUS WELL SEALED STORAGE

Storage type	Purpose	Rate m^3hr^{-1}	Generator type	Cost: Capital ($A)	Cost: Operating cents m^{-3}
Farm bin (50t)	Maintenance	0.5	Membrane	6,000-10,000	5-15
Shed (2,500t)	Maintenance	10	PSA	20,000-30,000	4-8
Silo (2,000t)	Purge	50	Burner	50,000-70,000	3-6
Shed (25,00t)	Purge	2,000	PSA	1M	4-8

Systems burning hydrocarbons, eg. propane, to remove oxygen from air, producing a low oxygen content exhaust, have been developed specifically for grain storage. Again similar systems have been in use for some years for fresh fruit preservation in CA. The burner systems are either based on an 'open flame' system (eg. Agrigas) or an internal combustion engine (eg. Agricage). Both are available commercially in sizes capable of treating substantial tonnages (> 2000t) by CA, but they have yet to gain wide acceptance.

Carbon dioxide-based atmospheres rely on supply of gas from off-site sources (dry ice, liquid delivery, pipeline). It appears unlikely that an on-site machine will be developed specifically to generate CO_2, although it is quite feasible in theory (eg by fermentation or combustion of coke in oxygen). Combustion of carbon-rich materials such as straw or biogas in air do not directly give more than about 15% CO_2 in nitrogen. With correct combustion and purification this can be used directly as a gas for making low oxygen CA. To provide gas suitable for making high-CO_2 atmospheres, >40% CO_2 this will require substantial enrichment, adding cost and complexity. The advantages of high-CO_2 CA are unlikely to be sufficient to compensate for this.

4. DISCUSSION

The foregoing has provided a brief summary of a large field of endeavour in grain storage research and practice. As can be seen there are very few major areas that need further research. Essentially we know what gas to use, what exposure times to allow, how to modify the storage and assess its suitability, what effects CA have on the commodity and how much gas is required. There is a range of methods to supply the gas used in the CA and the approach can be easily costed. It is a process ready for application.

Despite this, the lack of progress towards large scale adoption of CA technology in grain storage is striking. There are a few notable exceptions (eg. rice storage by BULOG in Indonesia). A number of factors are responsible for this in Australia and it appears unlikely that CA will be used except for specialist treatments, for example disinfestation of 'organic' grain, until these constraints are resolved. Until now the main factor has been the success and very low cost of applying phosphine in sealed systems. The material cost of this process is typically less than 10¢ per tonne in Australia, with small labour costs, and only recently have on-site CA generators become available to match this operating cost. If regulatory requirements on phosphine use become more demanding (eg. increased requirements for monitoring, actions required to reduce environmental phosphine, load etc.) the costs of CA may fall below those of phosphine in many situations in the near future. Another factor inhibiting CA use in Australia has been a belief that excessively long exposure times are required. The Australian grain industry now frequently uses exposures of a month with phosphine. This means that CA exposures even of a few weeks are quite feasible at high storage temperatures, CA treatments may even be faster than phosphine fumigations, especially when allowances are made for dosing and airing. Lack of sealed facilities certainly constrain CA use in many countries, but the technology is available to remedy this. The main problem with sealing stores is not the cost or technology so much as convincing the store owners or operators that sealing to an adequate standard is possible at all.

Over the next few years it appears likely that CA could become much more widely adopted, with the impetus for this change derived from the evolution of low cost methods of supply of CA gases coupled with a need to move away from chemically based control measures. In the longer term it is to be hoped that there will be further developments in ways of creating CA conditions in stores to make the process more attractive commercially and applicable in widely different economic circumstances.

CA technology is only one of the possible systems for disinfestation and preservation of grain in storage. However, it is one of the few that are likely to satisfy the developing requirements for low-cost, pest-free storages, without environmental hazards or residues on the commodity. We believe that the next decade will see much increased use of this technique.

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LES TECHNIQUES DE STOCKAGE DU GRAIN EN ATMOSPHERE MODIFIEE, ETAT ACTUEL ET PERSPECTIVES

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RESUME

Les techniques de stockage du grain en atmosphère modifiée sont disponibles dans tous leurs détails depuis presque vingt ans. Les procédures détaillées ont été publiées pour les grands magasins de stockage, les piles de sacs, les conteneurs et les petits tas de marchandises. Malgré tout cela, ces techniques doivent encore se faire connaître. Leur emploi est gêné par une série de préjugés concernant leur efficacité, leur besoin de structures étanches et d'expositions longues, ainsi que par le simple conservatisme des responsables. Cependant, elles apparaissent avoir un rôle indispensable à jouer lorsque l'absence de résidus après traitement devient une obligation. L'opinion étant de moins en moins favorable aux traitements chimiques, elles sont appelées à un avenir certain.

Les recommandations les plus courantes concernant les atmosphères pauvres en oxygène ou riches en dioxyde de carbone indiquent qu'il faut pratiquer une exposition d'au moins une semaine, et souvent de plus d'un mois dans certaines conditions. Ces recommandations sont ici révisées et la possibilité de réduire le temps d'exposition y est envisagée. On y décrit les nouvelles méthodes de production sur les lieux d'utilisation d'atmosphères contrôlées et de mélanges air/gaz inertes. Elles rendent ces techniques commercialement plus intéressantes et y sont inclus les brûleurs, PSA et systèmes d'échangeurs à membrane.