16 Controlled or Modified Atmospheres

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Introduction

Atmospheric manipulation for the protection of stored products such as grains has been researched extensively for more than 30 years (Adler et al., 2000; Calderon and Barkai-Golan, 1990; Jay, 1984; Navarro, 2006). Processes such as airtight or hermetic storage have been used successfully to maintain grain quality in South America (Argentina), the Middle East, India, and North Africa. Modified atmospheres (MA) or controlled atmospheres (CA) offer an alternative to the use of conventional residue-producing chemical fumigants for controlling insect pests attacking stored grain, oilseeds, processed commodities, and some packaged foods. These atmospheres also prevent fungal growth and maintain product quality.

The development of this technology has come about mostly over public concern about the adverse effects of pesticide residues in food and the environment. Although this method has become well established for control of storage pests, its commercial use is still limited to a few countries. More recent investigations have attempted to integrate modified atmosphere application into the 21st century version of raw product and manufactured food storage and transportation (Navarro 2006).

MA is proposed to serve as the general term, including all cases in which the atmospheric gases' composition or their partial pressures in the treatment enclosure have been modified to create conditions favorable for insect control. In a MA treatment, the atmospheric composition within the treated enclosure may change during the treatment period. In a CA treatment, atmospheric composition within the treated enclosure is controlled or maintained at a level and duration lethal to insects. The results are the creation of processes for managing food preservation that are residue-free, relatively safe to apply, and environmentally benign (Navarro 2006).

The purpose of this chapter is to discuss the concepts and variations of MA and CA, their impact on pests and on the quality of the product being treated, the structures where they may be considered for use, and their compatibility in commercial settings.

MA Hermetic Storage

A type of MA that can be applied for the protection of grain is *hermetic storage*, also termed *sealed storage* or *airtight storage* or *sacrificial sealed storage*. This method takes advantage of sufficiently sealed structures that enable insects and other aerobic organisms in the commodity or the commodity itself to generate the MA by reducing oxygen (O_2) and increasing carbon dioxide (CO_2) concentrations through respiratory metabolism. Respiration of the living organisms in storage (insects, fungi, and grain) consumes oxygen (O_2), reducing it from near 21% in air to 1 to 2%, while production of carbon dioxide (CO_2) rises from an ambient 0.035% to near 20% (White and Jayas 2003). This environment kills insect and mite pests and prevents aerobic fungi from growing (Weinberg et al. 2008). Elevated CO_2 and depleted O_2 levels will generally maintain stored grain quality for long periods of time. Grain with excessive moisture may be invaded by lactate-forming bacteria and yeasts (White and Jayas 1993). Hermetic storage has been in use for several thousand years preserving grains in airtight pots or containers (Adler et al. 2000). The key to successful hermetic storage is airtightness and control of condensation. In modern times, storage size has increased from small family storages to large bulks representing many producers or a portion of a country's total production. In the 1960s and 70s, large aboveground hermetic storage in some African and Asian countries was discredited because of severe condensation problems, particularly in metal structures (Navarro et al. 1994). Semi-underground storage has been used successfully in Argentina, Kenya, and Cyprus; Australia and Israel have successfully used bunker storage systems from the 1980s.

With recent improvements in materials and construction of flexible, nonporous bags and liners, a variety of size options offer protection for products from 25 to 1000 kg up to 10,000 to 15,000 tonnes (Navarro 2010). Commodities including cereals, oilseed grains, pulses, cocoa, and coffee can be stored safely for many months, maintaining high quality and limiting molds and mycotoxins. Plastic structures suitable for long-term storage systems, as well as intermediate storage of grain in bags or in bulk have been developed and applied.

Storage systems based on the hermetic principle include the following:

- Bunker storage in gastight liners for conservation of large bulks of 10,000 to 15,000 tonnes;
- Flexible gastight silos supported by a weld-mesh frame of 50 to 1,000 tonnes capacity for storage of grain in bulk or in bags;
- Gastight liners for enclosing stacks of 5 to 1,000 tonnes capacity, called storage cubes or Cocoons™, and designed for storage at the farmer-cooperative and small trader level or larger commercial and strategic storage facilities;
- Silo Bags of 200 tonnes capacity for on-farm grain storage directly in the field. This technique was originally used for grain silage, and involves storing dry grain in sealed plastic bags; and
- Small portable gastight containers of 25 kg to 2.5 tonnes, called SuperGrainbags™, which are suitable for seed storage and man-portable and bagged commodities. These structures enabled the application of modern MA technology worldwide to provide quality preservation and insect control.

CA Under Normal Atmospheric Pressure

Gas supply from pressurized cylinders – CA is a modified gas composition, usually produced artificially, and maintained unchanged by adding desired gases (CO_2 or nitrogen [N_2]), supplied from pressurized cylinders or other means. This supplementary introduction of gases is carried out when their concentration in the sealed container drops to below the desired level.

The objective of CA treatment is to attain a composition of atmospheric gases rich in CO_2 and low in O_2, or a combination of these two gases within the storage enclosure or treatment chamber. These set concentrations are maintained for the time necessary to control the storage pests. A widely used source for production of such atmospheric gas compositions is tanker-delivered liquefied CO_2 or N_2, when the target CA gas composition is <1% O_2 or high CO_2 concentration. For large-scale application of N_2 or CO_2, vaporizers are essential. These vaporizers consist of a suitably designed receptacle with a heating medium (electricity, steam, diesel fuel, or propane), a super-heated coil with hot water jacket, and forced or natural draught.

Combustible gases – Exothermic gas generators or gas burners are available for on-site generation of CAs. They work by combustion of hydrocarbon fuel to produce a low O_2 atmosphere containing some CO_2. Their CA composition is designed to allow the presence of approximately 2 to 3% O_2, with CO_2 removed through scrubbers. Several adaptations are required for use in the grain industry, i.e., tuning equipment to obtain an O_2 level of less than 1%; utilizing the CO_2 generated to full advantage; and removing excessive humidity from the atmosphere generated. Combustion of propane and butane yields approximately 13% and 15% CO_2, respectively. The CA generated is more toxic than a N_2 atmosphere deficient in O_2 because of the presence of CO_2. The combined effect of CO_2 and low O_2 results in greater insect mortality.

On-site N_2 generators – Commercial equipment, called pressure-swing adsorption systems, use the process of O_2 adsorption from compressed air passed through a molecular sieve bed. For continuous operation, a pair of adsorbers is provided that operate sequentially for O_2 adsorption and regeneration. Nitrogen at a purity of 99.9% can be obtained through regulation of inlet airflow; this method of N_2 generation is an expanding new approach in CA-generation technology. Equipment is now being manufactured that is rated to supply an outlet flow of 120 m^3/h at an outlet purity of 98% N_2.

Ozone – Ozone can be generated and used to kill insects, although it reacts with caulking in bins and may bleach grain. Ozone also lowers levels of microflora on seed. It is suggested for use in railcars at low temperatures and low humidity (McClurkin and Maier 2010). It is also effective in killing insects at 1800 ppm for 120 minutes and can be applied in specially modified augers (McDonough et al. 2010).

CA Under Altered Atmospheric Pressure

Vacuum or low pressures – In a low-pressure environment there is a close correlation between the partial pressure of the remaining O_2 and the mortality rate. Until recently this treatment could only be carried out in specially constructed rigid and expensive vacuum chambers. A practical solution has been invented that uses flexible liners. To achieve the low pressures in the flexible liners, sufficiently low pressures (25 to 50 mm Hg absolute pressure) can be obtained (using a commercial vacuum pump) and maintained for indefinite periods of time by continued operation of the pump.

High-pressure carbon dioxide treatment – CO_2 treatments can be significantly shortened to exposure times that may be measured in hours using increased pressure (10-37 bar) applied in specially designed metal chambers that stand the high pressures. Because of the high initial capital investment, these high-pressure chamber treatments may be practical for high-value products such as spices, nuts, medicinal herbs, and other special commodities.

Effects of CA on Insects Under Normal Atmospheric Pressure

Effects of low oxygen levels – Insects can tolerate low levels of oxygen for prolonged periods. Using N_2 to replace O_2 must result in O_2 being below 2%, preferably 1% for rapid death. This effect is reversed below 1% O_2 in N_2 where adult rice weevils, *Sitophilus oryzae* (L.) (Navarro et al. 1978) showed tolerance, increasing the lethal exposure time by apparently closing their spiracles. In particular, *S. oryzae* adults are killed more quickly at 1.0% O_2 rather than at 0.1 or 2% O_2 under the same conditions. *Tribolium castaneum* (Hbst.) in N_2 showed significant differences in adult mortality between 0.1 and 1.0% O_2 (Navarro 1978). Adults are generally most susceptible to treatment, and *S. oryzae* or *Rhyzopertha dominica* (F.) was found to be more tolerant than *Tribolium* spp. The lowest level of tolerance to lack of O_2 was attained around the 1% concentration level. Therefore, Annis (1987) concluded that O_2 levels of 1% are needed to kill insects in 20 days (Table 1).

Table 1. *Suggested provisional dosage regimes for control of all stages of the 12 most common insect species of stored grain, using modified atmospheres at temperatures between 20° and 29°C* (Navarro and Donahaye 1990).*

Atmospheric gas concentration	Controls most common grain insects including *Trogoderma granarium*	Exposure period
	yes/no	days
<1% O_2 (in nitrogen)	yes	20
Constant % CO_2 in air		
40	no	17
60	no	11
80	no	8.5
80	yes	16
CO_2 decay in air from >70 to 35%	no	15
Pressurized CO_2 at >20 bar	**	<0.35

* Data, except those on pressurized CO_2, compiled from Annis (1987).

Effects of high carbon dioxide levels – Elevated CO_2 levels cause spiracles to open resulting in insect death from water loss. Above 10% CO_2 spiracles remain permanently open. Toxic effects are entirely through the tracheae, not the hemolymph; CO_2 has direct toxic effects on the nervous system. In some cases, CO_2 can acidify the hemolymph leading to membrane failure in some tissues (Nicolas and Sillans 1989). Elevated, but sublethal CO_2 levels, for prolonged periods can have deleterious effects on insect development, growth, and reproduction (White et al. 1995, Nicolas and Sillans 1989). Atmospheres containing about 60% CO_2 rapidly kill stored-product insects. At 26°C, about 4 days of exposure would be sufficient to kill all stages (including eggs) of most stored-product insects (Table 1).

High carbon dioxide and low oxygen levels – Atmospheres with 60% CO_2 and 8% O_2 are very effective at killing internal seed-feeding insects, while low O_2 atmospheres are more rapid in killing external-feeding insects (Banks and Annis 1990). High CO_2 levels, even with 20% O_2,rapidly kill insects because of CO_2 toxicity. CO_2 levels must be at 40% for 17 days, 60% for 11 days, 80% for 8.5 days at temperatures above 20°C, or 70% declining to 35% in 15 days at 20°C (Annis 1987). Higher temperatures accelerate CO_2 toxicity as insect metabolism is elevated. Even low levels of CO_2 (7.5-19.2%) for prolonged periods sharply increase immature and adult mortality (White et al. 1995).

Effects of temperature and relative humidity on controlled atmosphere fumigation – Insect mortality increases more rapidly as temperatures rise and their metabolism speeds up. Cool temperatures slow rates of mortality while lower relative humidities (RH) hasten toxic effects, notably in high CO_2 atmospheres because of desiccation of insects (Banks and Fields 1995).

Development of insect tolerance to controlled atmospheres – Bond and Buckland (1979) were the first to show that stored-product insects have the genetic potential to develop tolerance to CAs, when they obtained a three-fold increase in tolerance to CO_2 by *Sitophilus granarius* (L.) after selecting for seven generations. Navarro et al. (1985) obtained a similar level of resistance for *S. oryzae* exposed to hypercarbia by selection over 10 generations. *Tribolium castaneum* populations were exposed to high levels of CO_2 (65% CO_2, 20% O_2, 15% N_2) (Donahaye, 1990a) or low levels of O_2 (0.5% O_2, 99.5% N_2) (Donahaye, 1990b) and 95% RH for 40 generations. Selection pressure in both bases was between 50% and 70% mortality each generation. At 40 generations, the insects exposed to high CO_2 levels had an LT_{50} (lethal exposure time to kill 50% of the test population) 9.2 times greater than nonselected insects. Insects exposed to low O_2 had an LT_{50} 5.2 times greater than nonselected insects. While these insects were able to adapt to extreme atmospheric composition to a moderate extent, the conditions used would not occur naturally.

CA Effects on Insects Under Altered Atmospheric Pressure

Effects of low pressures – Mortality of insects under low pressures is caused mainly by the low partial pressure of O_2 resulting in hypoxia (Navarro and Calderon 1979). The partial pressure of oxygen has a decisive effect on insect mortality, while no significant function could be attributed to the low pressure itself. At 50 mm Hg, partial pressure of O_2 is equivalent to 1.4% O_2, this being similar to the target O_2 concentration under a modified atmosphere obtained by N_2 flushing. Finkelman et al., (2004) showed that less than 3 days under 50 mm Hg at 30°C would control all stages of *Ephestia cautella* (Wlk.), *Plodia interpunctella* (Hbn.), and *T. castaneum*. The times needed to obtain 99% mortality were 45 hours, 49 hours, and 22 hours, respectively. The eggs of all three species were most resistant to low pressure.

Effects of carbon dioxide at high pressures – With CO_2 at high pressures (20 to 40 bar) all types of pests and their life stages can be killed within a short time. Generally, increasing the pressure reduces the lethal exposure time. *Lasioderma serricorne* (F.), *Oryzaephilus surinamensis* (L.), *T. castaneum*, *T. confusum* J. du V., *Trogoderma granarium* Everts, *Corcyra cephalonica* Stainton, *Ephestia elutella* (Hbn.), *E. cautella, P. interpunctella,* and *Sitotroga cerealella* (Oliv.) were exposed at a temperature of 20°C and carbon dioxide at 37 bar for 20 minutes, 30 bar for 1 hour, and 20 bar for 3 hours resulted in 100% mortality of all insects. Survivors of *T. confusum* were found after treatment with 10 bar for 20 hours. The rate of decompression of pressurized storages may also have an adverse impact on insect mortality. The relatively rapid control of pests in all stages of development is based on both the narcotic and acidifying effect induced by the high solubility of carbon dioxide in cell fluid, and on the destruction of the cells following the CO_2 pressure treatment during depressurization.

Effects of CA on Product Quality

Germination of seeds – Seeds below their critical moisture content are not significantly affected at high CO_2 or low O_2 atmospheres. However, with increasing grain moisture contents, CO_2-rich atmospheres could reduce the physiological quality of grain by interfering with the enzymatic activity of glutamine-decarboxylase. The adverse effect of CO_2 on germination of rice, maize, and wheat becomes more pronounced at temperatures higher than 47°C and, from observations carried out so far, this adverse effect may not be detectable at all below 30°C. If preservation of germination is of primary importance, the use of CO_2 free, low O_2 atmospheres is preferred if expected temperatures are significantly above 30°C.

Viability of corn stored under hermetic (148 days storage) and non-hermetic (120 days storage) conditions in the Philippines did not indicate significant changes between the initial and final samples (Navarro and Caliboso 1996; Navarro *et al*., 1998). In the same trials, viability of grain stored under hermetic conditions did not change significantly. To test viability of wheat stored under hermetic conditions in Israel, two trials were carried out with storage periods of 1,440 and 450 days only under hermetic conditions. Viability of wheat changed slightly from an initial 99% to 97% after 1,440 days, and from 97% to 91% after 450 days, respectively. In both trials, insect populations were successfully controlled and the average CO_2 concentrations ranged between 10% and 15%.

Product quality preservation – Donahaye et al. (2001) reported on quality preservation of 13.4 to 31.9 tonne lots of grain, stacked in flexible enclosures and stored outdoors for 78 to 183 days. The quality of the grain was compared with that of three control stacks (5.3 to 5.6 tonnes capacity) held under tarpaulins in the open for 78 to 117 days. Percent milling recovery and levels of yellowing in the gas-tight stacks showed no significant change. In a study on quality preservation of stored cocoa beans by bio-generated modified atmospheres, respiration rates of fermented cocoa beans were tested at equilibrium relative humidities of 73% at 26°C in hermetically sealed containers. The O_2 concentration was reduced to <0.3%, and CO_2 concentration increased to 23% within 5.5 days. The free fatty acid (FFA) content of cocoa beans at 7%, 7.5%, and 8% moisture content under hermetic conditions of 30°C remained below or close to 1% after 90 and 160 days of storage (Navarro et al. 2010).

Types of Structures in which CA and MA Have Been Used

Controlled atmospheres have been used in a wide array of grain storage structures. The most important consideration is that they must be airtight for long-term storage or relatively airtight for CO_2 or N_2 fumigation. Acceptable airtightness for CO_2 fumigation is determined by negative pressure testing and should at most hold a negative pressure from 500 pascals to 250 pascals in 10 minutes (Annis and van S. Graver 1990). Attempts have been made to predict gas tightness relative to leakage areas (Mann et al. 1999; Lukasiewicz et al. 1999). Provisional guidelines based on best estimates from a comparison of variable pressure tests are presented in Table 2 (Navarro 1999). The suggested times given in Table 2 were doubled for empty storages as an approximation to the intergranular airspace.

In-ground storage – Historically, in-ground storage was widely used worldwide to create hermetic storage where CO_2 was produced and O_2 consumed by respiration of grain and microflora. Its use was recorded from Spain to India and China, East Africa, and North America west of the Mississippi River (Sigaut 1988).

Bolted steel bins – Bolted steel bins are not airtight but they can be sealed for partially successful fumigation with CO_2. Alagusundaram et al. (1995) placed dry ice in insulated coolers under a CO_2 impervious plastic sheet above wheat 2.5 m deep in a 5.6 m diameter bin. CO_2 levels were 30% at 0.55 m above the floor where 90% of rusty grain beetles, *Cryptolestes ferrugineus* (Steph.) were killed; CO_2 levels of 15% at 2.0 m above the floor resulted in 30% mortality. A bolted, galvanized-iron silo (21.5

Table 2. *Provisional recommended ranges for variable pressure tests carried out in structures destined for gaseous treatments to control storage insects (Navarro 1999).*

		Variable pressure test decay time 250-125 Pa	
Type of gaseous treatment	Structure volume in cubic meters	Empty structure	95% full
		------------- min. -------------	
Fumigants	Up to 500	3	1.5
	500 to 2,000	4	2
	2,000 to 15,000	6	3
CA	Up to 500	6	3
	500 to 2,000	7	4
	2,000 to 15,000	11	6
MA, including airtight storage	Up to 500	10	5
	500 to 2,000	12	6
	2,000 to 15,000	18	9

tonnes) was sealed using a polyvinyl resin formulation sprayed onto joints from the inside. The silo was loaded with wheat into which cages of insect-infested wheat were introduced, and conditions monitored with thermocouples and gas sampling lines. Oxygen levels were reduced to <1% by purging with N_2, and similar levels were then maintained by a slow N_2 bleed for 35 days, after which the silo was emptied. All adult insects were dead but, as expected, some immatures survived. This was because the maintenance period was too short to ensure complete kill at the observed grain temperatures of <15°C (Williams et al. 1980).

Sealed steel bins – Airtight, galvanized-steel bins have been manufactured in Australia for the past 30 years and are commercially available (Moylan Silos 2011). Welded steel hopper bins can be modified for CO_2 fumigation for a few hundred dollars. Carbon dioxide from dry ice must be recirculated through the grain and a pressure relief valve installed to the bin. The top and bottom hatches must be gasket sealed. After 10 days at 20°C, 75% of applied CO_2 was retained while 99% of the caged C. *ferrugineus* were killed (Mann et al. 1999).

Concrete grain elevators – Carbon dioxide fumigation of grain has been successful in concrete elevators holding 209 tonnes of wheat. The bottom hopper was sealed and the grain purged with CO_2 for 4 hours (1 metric tonne of CO_2) and additional gas is added as needed. All caged test insects were killed (White and Jayas 2003). A large installation for the application of CO_2-based CA was installed to treat more than 200,000 tonnes of rice annually in flat bins each of 5,000 tonnes capacity in Mianyang, China.

Airtight grain bags – The use of hermetic grain storage in flexible structures is growing throughout the world. Although some structures are not airtight and are easily punctured (Darby and Caddick 2007), new materials offer satisfactory results with high levels of gastightness (Jonfia-Essien et al. 2010; Rickman and Aquino 2004).

One method using airtight bags for 25 kg to 1,000 tonne masses of product is now commercially available as Supergrainbags™, Cocoons™ (Figure 1), MegaCocoon™ and TranSafeliners™ The bags rapidly produce hermetic storage (Jonfia-Essien et al. 2010, Navarro et al. 2007) and are currently used in 82 countries.

Silobag is another sealed system used for temporary storage of dry grain and oilseeds in South America. Each silobag can hold approximately 200 tonnes of wheat and is simple to load and unload with available handling equipment (Bartosik 2010).

Figure 1. *Hermetic storage of150 tonnes of corn in a Cocoon, Rwanda.*

Railcars – Hopper railcars have been treated in-transit with phosphine gas for flour and wheat in Australia and North America (Eco2Fume 2003). Carbon dioxide fumigation requires a much greater level of air tightness than phosphine fumigation. Efforts have been made to seal a railcar containing 90 tonnes of wheat. Even after sealing top hatches with CO_2-impermeable plastic and caulking the bottom hoppers, 118 kg of dry ice produced only 21% CO_2 at 1 day, a level too low for insect control (Mann et al. 1997). If the railcar had been moving, gas loss would have been rapid (Banks et al. 1986).

Commercial Use

Numerous MA and CA systems have been developed over the years to manage insect pests and microflora associated with stored products; however, their general commercial use remains somewhat limited (Adler et al. 2000). Exceptions are for organic products where use of fumigants is not possible because of residues; hermetic storage in plastic structures with application of MA is the preferred choice (Navarro 2006).

Vacuum storage – Vacuum storage or the use of low pressure in flexible PVC chambers has been demonstrated as an effective means for maintaining quality and controlling insect pests in smaller volumes (approximately 50 to 60 tonnes) of peas, beans, wheat, corn, and sunflowers for extended lengths of time (Finkelman et al. 2002; 2003). In these applications, products in bags or totes are placed within the liner, vacuum is applied, and the liner shrinks over the bags. Successful control times have been demonstrated at 55 mm of Hg similar to phosphine (7-day exposure) at temperatures averaging 30°C and humidity averaging 65% RH. Problems can easily be detected using pumps equipped with control panels and sensors, thus, product monitoring becomes unnecessary. These types of treatments are used for high-value commodities because the treatment is nontoxic and relatively quick (highly beneficial in the event of quarantine needs).

Hermetic storage – When placed in sealed airtight storage, commodities and the insects and aerobic microflora that exist within them respire, consuming O_2 and producing CO_2. This modified atmosphere technology has been utilized to a great extent for durables such as grains. Hermetic grain bags (Africa, Argentina, Asia, Australia, North and South America, Middle East) and sealed bunker storage (Australia, U.S., Middle East) have been implemented into commercial application to various extents.

Bunker storage, having designed storage capacities to more than 10,000 tonnes, is established in permanent locations with a prepared base (usually asphalt or compacted soil with a convex profile) and an airtight cover. This type of storage has been used extensively in Australia, Argentina, Israel, and Cyprus (Adler et al. 2000). While low moisture content, high temperature grain supports this type of storage, condensation can remain problematic if the grain is stored with cones or ridges (Navarro et al. 1994). Sealed bunker storage has also been demonstrated as an effective means for utilizing CA or conventional fumigation where the bunker is sealed and flushed with N_2 or CO_2 .

A major challenge that South America is facing is to minimize quality and quantity losses, and improve food safety in view of the shortage of permanent storage capacity. As a result, the silobag system for temporary storage of dry grain and oilseeds has been adopted. During the 2008 and 2010 harvest seasons, more than 33 million and 43 million tonnes of grain were stored, respectively, in these plastic bags in Argentina. Commodities included corn, soybean, wheat, sunflower, malting barley, canola, cotton seed, rice, lentils, sorghum, beans, and even fertilizers. The silobag technology is also being adopted in other countries such as the United States, Australia, Bolivia, Brazil, Canada, Chile, Italy, Kazakhstan, Mexico, Paraguay, Russia, South Africa, Sudan, Ukraine, and Uruguay (Bartosik 2011 personal communication).

Controlled atmospheres – Nitrogen and CO_2 have been used as agents for controlled atmospheric storage for many years. Carbon dioxide has been considered to be more efficient than N_2 due to the concentrations necessary for control and the level of gas tightness of the structure being used. A CO_2 concentration of about 60% can provide 95% control of most stored-product insect pests at 27°C (Jay 1971), while N_2 use requires interstitial O_2 levels to be reduced to 1% or less. Considerable efforts to improve bin sealing of storage bins have been made (Mann et al. 1999) which in turn facilitates ease in gas application and retention. Mann et al. (1999) demonstrated that CO_2 generated from dry ice and circulated with a vacuum pump at a concentration of 51% caused 100% mortality of *C. ferrugenius* after 10 days at 20°C. Carbon dioxide can also be added to bulk stored products as compressed gas. White and Jayas (1991) demonstrated that by circulating CO_2 released from compressed cylinders, high mortality of several stored-product arthropod pests could be achieved within 14 days. They found that bin sealing was crucial to maintain efficacy especially when commodity temperature fell below 20°C, and that utilizing pressure testing techniques (Banks and Annis 1980) is a useful means of determining a bin's seal.

Nitrogen production has also changed considerably over the years. Pressure-swing absorption systems have proven successful where a 13,660 m^3 bin can be purged to <1.0% O_2 in 7 days. Appropriate sealing allows for accurate calculation for additional gas application required to compensate for gas loss due to sorption, as well as pressure cycling caused by pressure change (Cassels et al. 2000). It also ensures gas concentration can be maintained for appropriate times. Liquid N_2 can be used for topping up the controlled atmosphere, but can cost twice that of other sources. Although CA treatment of grain is an old and proven technology, its applications remained limited. A recent development has been reported by Clamp and Moore (2000), in which N_2 supplied as a bulk liquid under pressure was used to treat 1,800 tonne bins. Since the N_2 treatment was commissioned in 1993, more than 300,000 tonnes were treated in the Newcastle facilities as of 2000 (Clamp and Moore, 2000).

Nitrogen also can be easily generated using molecular membrane generators. These are capable of purging vertical grain storages of 120 tonnes capacity within 3 hours (Timlick et al. 2002). By maintaining a slight positive bin pressure, concentrations within a sealed commercial storage could be maintained (compensation for leakage) and insect mortality was significant after 14 days at 17°C.

In terms of efficacy and efficiency, there is not much difference between using CO_2 over traditional fumigants such as phosphine. Nitrogen has been considered unsuitable for bulk commodity treatment at export position because the length of time required for significant mortality of the pests in question is too long. Effective management procedures can allow for N_2 use when temperatures are appropriate. All require effective sealing and monitoring and efficiency is directly correlated to temperature. While caution is necessary when utilizing any product as an atmospheric control, there are no residues of concern when utilizing MA. Aeration after treatment is of less concern, allowing for outturn of product in export position minimizing concerns for worker safety.

Flexible liners, loading and unloading equipment, nitrogen generators, or pressurized CO_2 (Figure 2) are commercially available. Equipment can be installed, maintained, and replenished with product on site.

Figure 2. *Application of high pressure CO_2 for the dry fruit industry in Turkey.*

Maintenance of sealing of hermetic storage has proven a challenge at times. Large bunkers and grain bags in Australia often have sealing breached by birds pecking holes in the liner. In Canada, deer often break the seals of hermetically stored grain in bags. Consequently, focused research on liner integrity may be of use in these types of situations.

Discovery of breached seals during CA treatments can be difficult to remedy, underlining the necessity of performing pressure testing before application.

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