AN OVERVIEW OF THE PRESENT STATE OF CONTROLLED ATMOSPHERE STORAGE OF GRAIN IN CHINA

LU QIANYU

Department of Grain and Oil Storage, Zhengzhou Grain College, Zhengzhou, Henan, Peoples' Republic of China.

Abstract: Controlled atmosphere (CA) technology is widely used in China in various forms for the preservation of stored grain. The airtight enclosures required for the process are made in several ways: by covering the grain surface with polyethylene sheet which is then fixed to the walls previously treated with asphalt, by completely enclosing the grain bulk in PVC sheet or, for small quantities, by sealing the grain in polyethylene/polyester laminated film (skinpacking). Carbon dioxide and simple hermetic storage processes are commonly used to provide the controlled atmosphere. A mobile unit for producing suitable atmospheres has been developed. This unit, containing cultures of microorganisms, is connected to the sealed system and reduces the oxygen content through the respiration of the microorganisms. Nitrogen production using exothermic inert-atmosphere generators and molecular sieve air separation systems are under investigation.

Rates of oxygen reduction under hermetic conditions and the influence of controlled atmospheres on grain quality and mould growth have been investigated. CO_2 at 80% inhabits the growth of moulds and yeasts and can preserve quality of stored rice for six months through the summer. It is preferable to combine CA treatment with reduction of temperature below 20°C to obtain the best storage conditions.

1. INTRODUCTION

Controlled atmosphere (CA) techniques have been adopted as the main methods for grain storage in large stores in China. CA systems are particularly acceptable as they either minimise the quantity of fumigant used or eliminate its use completely.

Two main problems must be overcome during the development of CA technology: how to create airtight enclosures and how to create suitable atmospheres. It is also necessary to determine the effect of CA storage on the quality of the various commodities and the optimum concentration of the various gases involved, both against pests and to preserve quality and for safety reasons. These problems have been studied in various regions in China. Some of the results of these studies are described in this paper.

Generally, it has been found that CA technology is convenient and cheap and that it may be applied effectively to the storage of many kinds of grain. It may also be used during transportation of grain, its sale to the consumer and even for the storage of medicinal materials and various native products. It can also be used as an emergency storage for grain of excessive moisture content which cannot be dried at once.

2. DEVELOPMENT OF CA TECHNOLOGY

2.1 Sealing of grain storages for CA use

2.1.1 <u>Sealing of the grain surface with polyethylene sheet ('one-side sealing')</u>. This method is suitable for the sealing of stores in which the grain is loaded in bulk. The walls and floor of the storage are rendered airtight by painting with asphalt. Polyethylene film is spread over the surface of the grain pile and sealed with wax into a trench in the top of the wall of the store (Fig. 1). The method has been widely used for the storage of bulk grain and is always used in large stores.

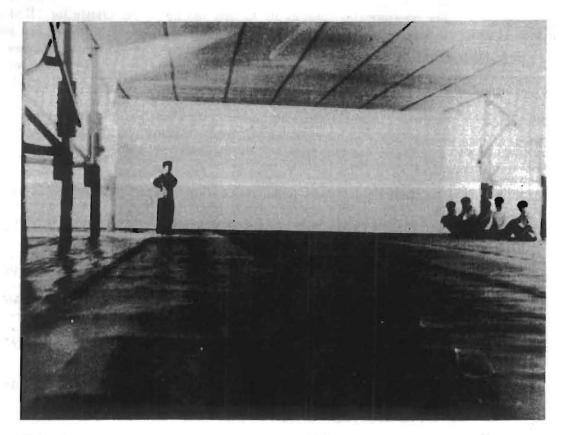


Fig. 1. Grain covered with PVC sheeting in a large store ('one-side sealing')

16

2.1.2 <u>Complete sealing in PVC ('six-side sealing')</u>. In this method the grain bulk is completely enclosed in PVC membrane. The enclosure is made in the following steps:

(i) The cover is made of 0.23mm thickness PVC film. The cover should be 40 cm larger than the stack.

(ii) Any leaks in the cover are patched or mended using an adhesive made of dichloroethane and perchloroethane (4:1).

(iii) Straw bags are placed as dunnage at the bottom of the stack (above the PVC groundsheet) and either straw or jute bags are laid on the surface of the stack.

(iv) The enclosure is made around the stack using a portable high frequency welding machine to seal the cover and groundsheet together.

The method is primarily used for storing various types of grain in cities (Fig. 2).

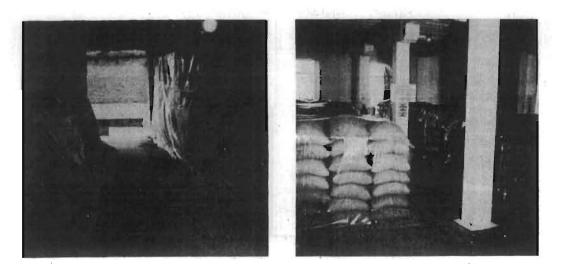


Fig. 2. Enclosing bag stacks of grain in PVC film ('six-side sealing').

2.1.3 <u>Skin-packing</u>. Packs of 2-20kg capacity are made for rice and other grains with polyethylene or polyethylene/polyester film using either natural reduction of oxygen, vacuum or the carbon dioxide exchange method (Fig. 3). When CO₂ is used with rice the pack becomes rigid in 3 hours. The method is now used for storing various products (e.g. peanuts, "green grain", red beans, sesame seed) in cities for direct supply to consumers. The stored materials can be kept in this way for a year. 2.2 Methods of generating and maintaining controlled atmospheres

2.2.1 <u>Natural reduction of oxygen in an airtight storage</u>. The grain grain bulk is enclosed in a plastic membrane. The grain respiration in the enclosure creates an oxygen-free environment, thus preserving the grain. The rate of reduction of oxygen is much slower for aged grain than for fresh grain. The moisture content of paddy or polished rice stored in this way should be 14.6 - 16%.

2.2.2 <u>Using CO₂ or N₂ from gas cylinders</u>. CO₂ or N₂ are supplied in steel gas cylinders. The gases are introduced at the base of the grain bulk, displacing the air in the bulk. The gas concentrations are maintained at 40-85% for CO₂ and 98-99% for N₂. This system provides excellent control of the activities of insects and preserves the grain in good condition for much longer than with storage in normal air atmospheres.

2.2.3 Methods of nitrogen generation for CA use.

 (i) <u>Combustion of hydrocarbons</u>. Gas may be generated from combustion of hydrocarbons giving a 98.5% N₂, 1.5% O₂ mixture.
Generators of this type are now used for CA storage.

(ii) <u>Molecular sieve absorption</u>. The system is based on the seperation of oxygen and nitrogen from air using multiple layers of Type 4A or 5A molecular sieve and calecite (*sic*) or natrolite. Seperation is achieved utilising the difference in diffusion rate of oxygen and nitrogen within the extremely small pores of the materials. The system (Fig. 4) gives 95-98% N₂ and can give a low oxygen atmosphere in 4-5 hours, with recirculation of the atmosphere through the machine.

2.2.4 <u>Utilisation of microorganisms to remove oxygen</u>. A 'culture box', containing microorganisms and culture medium, is connected to the grain bulk in an airtight enclosure (Fig. 5). The respiration of the microorganisms reduces the oxygen content of the bulk to a level which controls the growth of pest insects.

For use with large bulk storage bins, the culture box is installed in a mobile apparatus (Fig. 6).

3. RESEARCH STUDIES ON CA STORAGE OF GRAIN

3.1 Rate of natural reduction of oxygen.

In a grain bulk kept under airtight conditions, the oxygen content gradually decreases while the CO₂ content rises to a certain limit. The rate of change and the range of variation of the CO₂ and O₂ concentration is determined by grain type and the temperature

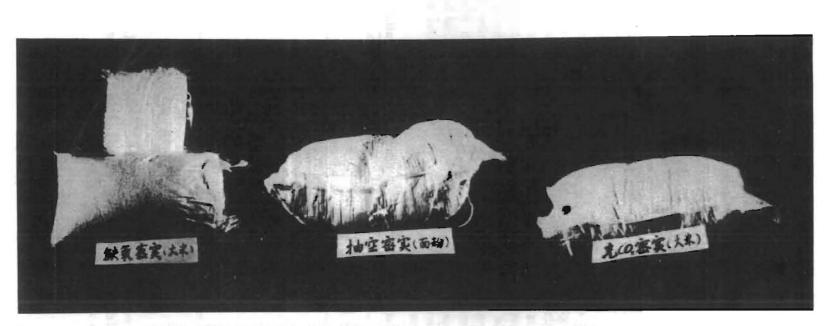


Fig. 3. Skin-packing of (a) rice under hermetic storage, (b) wheat flour in vacuum and (c) rice under CO_2 .

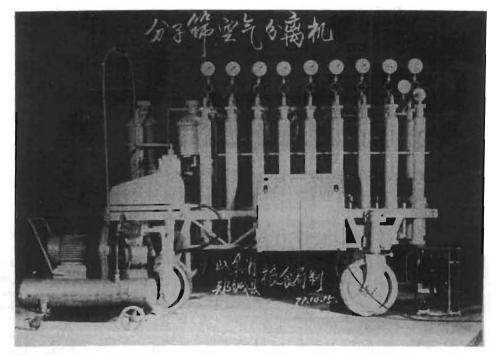


Fig. 4. A molecular sieve machine for separation of oxygen and nitrogen from air.

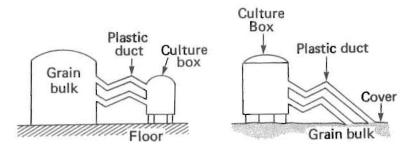


Fig. 5. Connection of a 'culture box', containing microorganisms, to grain bulks in airtight enclosures for a stack (left) or a plastic-covered grain bulk (right).

and moisture content of the bulk. The rate of reduction of oxygen content is greater at greater moisture contents (Figs. 7 and 8). 3.2 Studies on the growth of microorganisms.

CO2 can control the growth of moulds. The growth of both anaerobic and aerobic microorganisms is substantially inhibited if the CO2 content exceeds 80% (Table 1).

Under 80% CO₂ rice is in a dormant state and all species of insect are killed. Thus, in summer, grain bulks may be kept without moulding and heating and free of insects. If the grain moisture

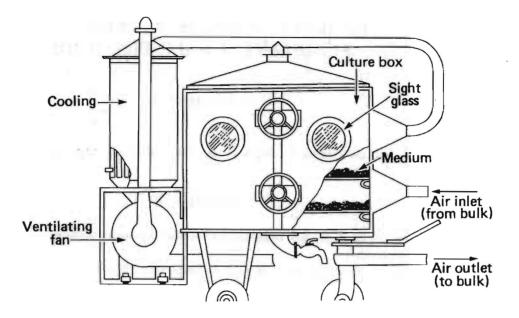


Fig. 6. A mobile apparatus, incorporating a 'culture box', for CA storage of grain in large bulk bins.

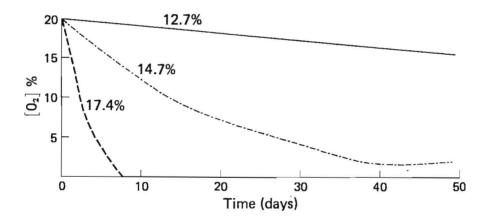


Fig. 7. Variation in the rate of change of oxygen content with moisture content for non-glutinous long grain rice under hermetic storage conditions.

content is >16% or there is condensation at the grain surface, moulding may occur under natural reduction of oxygen (hermetic storage). This may cause the plastic film enclosures or bags to swell up. The moulds found under these conditions are always either *Aspergillus* spp. or *Rizopus* spp. Thus, to ensure that rice may be stored safely in summer, it is recommended that the moisture content be kept below 16%. If the moisture content exceeded 16%,

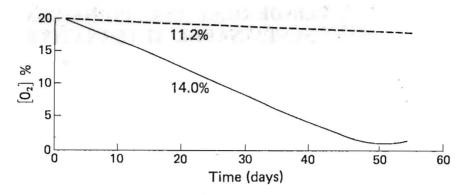


Fig. 8. Variation in rate of change of oxygen content with moisture content for wheat under hermetic storage conditions.

TABLE 1.

Areas of various colonies (cm^2) grown from a single spore under various CO₂ levels.

| Species | % CO2 | | | | | | | |
|-------------------------|-------|-----|------|------|------|------|--|--|
| - | 90 | 80 | 60 | -40 | 20 | 0 | | |
| Aspergillus candidus | 0 | 0 | 0 | 1.0 | 1.2 | 3.2 | | |
| A. flavus | 0 | 0 | 0 | 2.6 | 2.4 | 7.8 | | |
| A. niger | 0 | 0 | 1.4 | 1 | 1.0 | 5.4 | | |
| A. versicolur | 0 | 0 | 0 | 0.16 | 0.16 | 1.44 | | |
| Penicillium sp. | 0 | 0 | 0 | 0 | 0.16 | 7.7 | | |
| Saccharomyces sp. | 0.49 | 2.6 | 10.2 | 5.3 | 9.0 | 32.4 | | |

dew may form at the surface of the bag stack and moulding may occur when the stacks are stored under the natural hermetic storage system. The plastic covers may balloon out (Fig. 9). Interestingly, it has been found that the mould occurrence varies with season under hermetic storage conditions. The quantity of mould rises as the grain temperature increases and falls again when the grain temperature falls (Fig. 10).

3.3 Studies on grain quality.

The quality of stored grain can be preserved fairly well for six months if the CO₂ content in the store, initially at 80%, can be maintained above 70%. This is particularly so if the temperature is kept below 20°C as well. After storage over a summer season, the cooking quality of rice is as good as fresh grain (Table 2). Under hermetic storage conditions in summer, despite the high



Fig. 9. Mould growing on the surface of bags of rice stored at > 16% m.c. (left). Ballooning of the stack cover with rice stored at > 16% m.c. (right).

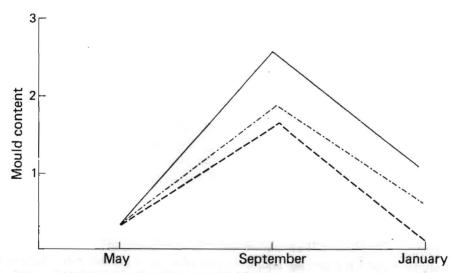


Fig. 10. The variation in mould content with season of rice stored in hermetic conditions.

prevailing temperatures, the grain quality does not deteriorate obviously, although various degrees of starch aging may take place.

The effect of the gas composition of the storage atmosphere on grain quality (Table 3) is much less than that of temperature. In experiments on rice stored under 98.5% CO₂, 1.5% O₂ at various temperatures it was found that temperature influenced the quality even when kept under CA. Aging of rice still occurs after storage

TABLE 2.

Variation in quality of rice stored under various CO₂ atmospheres for 6 months (temperature 13-20°C, moisture content 16.2%)

| Storage CO2% | atmosphere 02% | Cooking qualities | Acidity of water extract (ml N ROH/ 10 g d.m.) | Fat acidity (mg KOH/ 100g d.m.) | Viscosity (c.st.) | |
|-----------------|-------------------|----------------------|---|--|----------------------|--|
| 0 | 21 | 50 | 3.17 | 29.4 | | |
| 75-85 | 3-5 | 93 | 0.7 | 81.9 | 14.4 | |
| 85-95 | 1-3 | 95 | 0.7 | 82.8 | 15.1 | |
| Original | value | 100 | 0.7 | 57.4 | 16.4 | |

in summer with temperatures reaching 35°C. If the temperature is kept below 25°C the quality is maintained better under CA conditions. It is evident that CA storage is superior to ordinary storage (Figs. 11, 12).

3.4 Studies on Skin-Packing

Polyethylene/polyester composite films made in China are used for sacks of high grade rice of ca. 15.5% moisture content. Rice stored in these sacks at the standard temperature, 20°C, can be held for one to two years without degradation of quality from insects, overheating and other deterioration. The ageing of the rice is retarded.

It is claimed that the best storage atmosphere is made by creating a vacuum in a sack and replacing this vacuum by CO₂. The second best system is to replace the air directly by CO₂. These methods give a skin-packed product. Filling with nitrogen only does not give the skin-packing effect and is inferior, but still better than simple airtight storage. With simple airtight storage the packing film shrinks onto the grain as the CO₂ produced in the pack is absorbed. This takes at least 24 hours. Simple airtight storage is less convenient to use than the vacuum packing method.

It is found that the lower the temperature, the better the quality of the stored grain.

The quantity of CO₂ taken up in the skin-packing method has been investigated. Over 50 bags of 16 x 24 cm polyethylene/polyester film were filled with Grade II rice of 15.1% moisture content. The air in the bags was evacuated with a vacuum packing machine. The packs were then sealed and held at 12° C for 4 to 5 days. After

TABLE 3

Variation of quality of rice under various atmospheres for 3 and 8 months.

| | Natural oxygen- | | | | CO 2 | | | Air | |
|------------------------|---------------------------------------|-------|--------|--------|---------------|---------|-------|--------------------|-------------|
| | deficient atmosphere | | | e | | | | | |
| | init- | after | | | after | after | Init- | after | after |
| | ially | 3 | 8 | ially | | 8 | ially | 3 | 8 |
| | | mths | mths | | mths | mths | | mths | mths |
| Acidity of | -12 | 8 | | | | | | | |
| water extract | | | | | | | | | |
| (m1 N KOH/ | | | | | | | | | |
| 10g.d.m) | 0.7 | 1.1 | 0.62 | 0.7 | 1.8 | 0.37 | 0.7 | 0.65 | 0.40 |
| Fat acidity | | | | 10 0 V | 34-41-45-6998 | 10 10 E | | - CO. 10 - 1097779 | |
| KOH mg/ | | | | | | | | | |
| 100g.d.m. | 7.4 | | 73.1 | 7.4 | | 58.4 | 7.4 | | 45.2 |
| Hardness | | | | | 1 | | | | |
| (kg/kernel) | 4-7 | | 4-7 | 4-7 | | 3-6 | 4-7 | | 4-7 |
| (%) | 76 | | 74 | 76 | | 84 | 76 | | 79 |
| Iodine-Blue | | | | | | | | | ., |
| value | di s | | | | | | | | |
| (transmission, | | | | | | | | | |
| (ciulibilitititi %) | 53 | 77 | 71 | 57 | 78 | 68 | 53 | 67 | 64 |
| Specific | | | 11 | 51 | 70 | 00 | | 07 | |
| viscosity | . 11 | | | | | | | | |
| | | | | | | | | | |
| (E ₂₀ °C) | 1.71 | 2.06 | 1.80 | 1.82 | 2.06 | 2.22 | 1.71 | 1.85 | 1.94 |
| Amylogram | | | | | | | | | |
| Gelatinizatio | n | | | | | | | | |
| temperature | 83 | 84 | 81 | 83 | 85 | 80 | 83 | 85 | 81 |
| (°C) | 00 | 0.1 | 01 | 00 | 0,0 | 00 | 00 | 0,0 | 01 |
| Temperature | | | | | | | | | |
| of peak | | | | | | | | | |
| viscosity (°C | 1) 93 | 94 | 89 | 93 | 94 | 89 | 93 | 94 | 89 |
| Peak viscosit | · · · · · · · · · · · · · · · · · · · | 74 | 07 |)) | 74 | 0) | 10 | 74 | 0) |
| (E.U.) | -y 680 | 780 | 790 | 730 | 950 | 1000 | 680 | 860 | 860 |
| Final temp. | 000 | /00 | 7.70 | 150 |))(| 1000 | 000 | 000 | 000 |
| of viscosity | 97 | 98 | 95 | 97 | 89 | 96 | 97 | 98 | 96 |
| (°C) | 11 | 70 |)) | 21 | 09 | 90 | 21 | 70 | 70 |
| | | | | | | | | | |
| Final point | | | | | | | | | |
| of viscosity | 540 | 500 | 630 | F(0) | 720 | ((0) | E/.0 | 660 | 660 |
| (B.U.) | 540 | 590 | 020 | 560 | 720 | 660 | 540 | 660 | 000 |
| Cooking | | | | | | | | | |
| qualities | | | - | | | - | | | - |
| Lustre | | | 5 | | | 5 | | | 5 5 5 |
| Taste | | | 5 5 | | | 5 | | | 5 |
| Freshness | | | 5 | | | 4 | | | 5 |
| Cohesiveness | _ | | 4 | | | 4 | | | 4 |

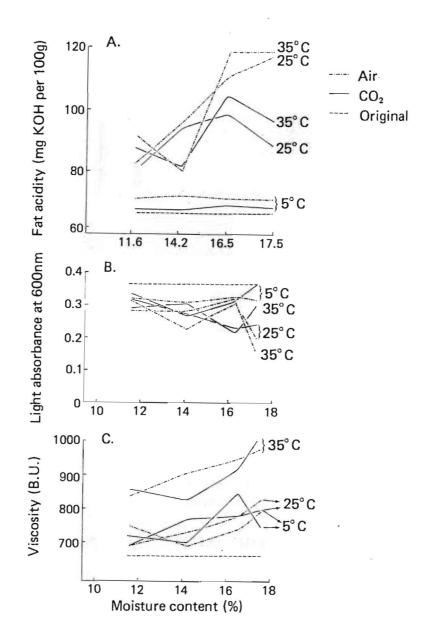


Fig. 11. (A) Variation in free fatty acid content in rice stored in air and CO_2 at three temperatures. (B) Variation in iodine-blue reaction of rice starch in rice stored in air and CO_2 at three temperatures. (C) Variation in paste viscosity from rice stored in air and CO_2 at three temperatures.

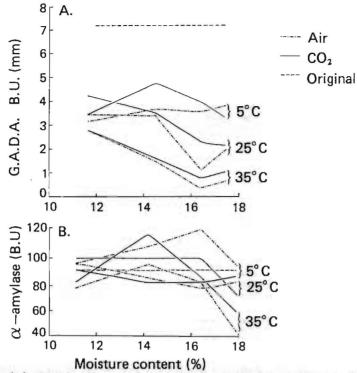


Fig. 12. (A) Variation in G.A.D.A. in rice stored in air and CO_2 at three temperatures. (B) Variation in α -amylase content of rice stored in air and CO_2 at three temperatures.

checking for any leaks in the film or its sealing, CO₂ was admitted to each pack through a flow meter. The quantity of CO₂ taken in was calculated from the time taken to refill the pack.

The quantity of CO_2 absorbed averaged 73 ml kg⁻¹. After allowance for diffusion through the packing film, this corresponds to an absorption of 69 ml CO_2 kg⁻¹. In Japan, where polyethylene/polyamide films are used, the absorption is reported to be 70 ml CO_2 kg⁻¹, a value close to that we observed.

4. OUTLOOK

CA techniques were initially applied to rice storage through the summer. This successful technique has been unanimously welcomed by personnel engaged in grain storage. Application of the hermetic storage technique using plastic films is inexpensive and is gradually being extended to the storage of maize and wheat. In state-owned or commercial storage in large cities, CA storage using either natural oxygen depletion or filling with CO₂ is widely adopted. Both the 'one-side' and 'six-side' sealing systems are used. The use of CO₂ seems preferable to filling with N₂. The use of multiShanghai Grain Research Institute, 1982. Studies on CO₂ absorption by rice and its quality change. (unpublished report). Shanghai Grain Research Institute, 1982. Studies on new storage

Shanghai Grain Research Institute, 1982. Studies on new storage techniques of sealed packaging of grain. (unpublished report).
Xiang Qi, 1974. Analysis of white mould in anaerobic storage of rice. Grain and Oil Science and Technology 1, 10-22.
Xiangtan Prefectural Grain and Oil Company, 1976. Experiments on

Xiangtan Prefectural Grain and Oil Company, 1976. Experiments on enriched nitrogen grain storage using a molecular sieve. Sichuan Grain and Oil Science and Technology <u>4</u>, 32-3.

t Editor's Note: These references are not cited in the text. The editor is grateful to Dr R. Conroy for translating the references into English from Chinese.