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EVALUATION OF LARGE, MODERN WAREHOUSE STORAGES DESIGNED AND CONSTRUCTED FOR APPLICATION OF CARBON DIOXIDE

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ABSTRACT

Warehouses for controlled CO₂ storage with a total capacity of 45,000 tonnes were constructed at Mianyang, where field experiments were successfully carried out. This paper describes the construction techniques, CO₂ supply and distribution system, auto-monitoring system, security and safety facilities, sealing materials, gastightness test techniques and field experiments. The results showed that design and construction techniques were reasonable. The pressure decay half-life from 500 Pa to 250 Pa, reached 12 minutes and thus effectively ensured maintenance of the concentration of CO₂. Automatic supply and distribution of CO₂ as well as monitoring were carried out during the whole process. The field experiment proved that both phosphine susceptible and resistant strains of *Sitophilus zeamais*, *Rhyzopertha dominica* and *Tribolium castaneum* had been effectively controlled to achieve complete kill with an exposure for more than 14d to CO₂ at concentrations within the range of 35%~75%. After incubating the mixed samples under different culture-conditions for 42d, no live adults appeared. There were also no significant changes in the level of microorganisms in the grain stored under CO₂. After 10 months storage, under CO₂, grain quality of the newly harvested grain with safe moisture content and good quality, was compared with grain of similar qualities but under conventional storage. The grain quality under CO₂ was better than the conventional storage and remained stable after unsealing.

INTRODUCTION

With the continuous progress of technology and advances in the quality of life, people care more about the protection of the environment, and consequently the demand for “green food”, which is of high quality and without chemical contamination, is increasing rapidly. The current grain storage technologies are developing towards an integrated way to reduce the use of chemical pesticides, including the use of low-temperature storage, controlled atmosphere (CA) techniques and biological control. The controlled CO₂ technique involves flushing CO₂ into

well-sealed warehouses so as to change the storage atmosphere, to control pests, to inhibit mold activity, and delay grain aging.

The first modern warehouses with controlled CO₂ were constructed at Mianyang, China in 2000, for a total storage capacity of 45,000 tonnes and consist of several bins with a capacity of more than 5,000 tonnes for each. After the first-period construction, experiments were carried out to compare them with conventional storage.

CONSTRUCTION OF THE CA WAREHOUSES

Construction Techniques

Condition of the warehouses

Warehouses with controlled CO₂: There are 5 horizontal warehouses consisting of 2 bins each, with dimensions: 24m width_96m length_7.8m height. (6 m height of grain bulk). Total capacity is 45,000 tonnes, with 5,000 tonnes capacity of each bin.

Control Warehouse: consists of one horizontal bin with the same dimensions as the above, but in which conventional storage was carried out as control.

Sealing Material

Based on the requirements of controlled CO₂ warehouse, several materials were tested and compared, with regard to flexibility, texture, resistance to extreme temperature and deterioration, resistance to ultraviolet radiation, non-contaminant or non-toxic content, durability, easy of use, low air-permeability, good adhesive ability, and with reasonable price.

Locations and Methods for Sealing

- According to the original design, the following steps were carried out:
- the windows and venting pipes were equipped with air-tight and heat-preservation facilities as well as axial fans to the windows
- the interior walls of the warehouse were brushed with Coating A
- sealing of the walls, top, and floor of the warehouses, was made, with each bonding point into camber of 150 mm
- highly elastic materials were filled into the gaps of the chambers
- all the openings of the warehouses were sealed, including the inlet holes, outlet holes, vent openings, axial fan openings, the CO₂ supply openings were checked, as well as the bonding point of lines and other openings.

Air-tightness of the Warehouses under CO₂

The pressure decay half-life of the warehouses with CO₂ reached more than 12 minutes with a decline from 500Pa to 250Pa, while the control only lasted about 40 seconds for the same pressure decay. Tests indicated that CO₂ concentration could effectively be ensured by a one-time introduction of CO₂.

Assembly of Equipment for Warehouses with CO₂

The key point in the CO₂ storage technique was the assembly of various equipment. In the construction phase, a large-scale central CO₂ supply and distribution system was initially set up. At the same time automatic gas monitoring, safety and security systems for use with the CO₂ were developed and applied (Fig. 1).

CO₂ supply and distribution system

The CO₂ supply and distribution system is used to store the liquid CO₂ safely, vaporize and supply the CO₂ when necessary.

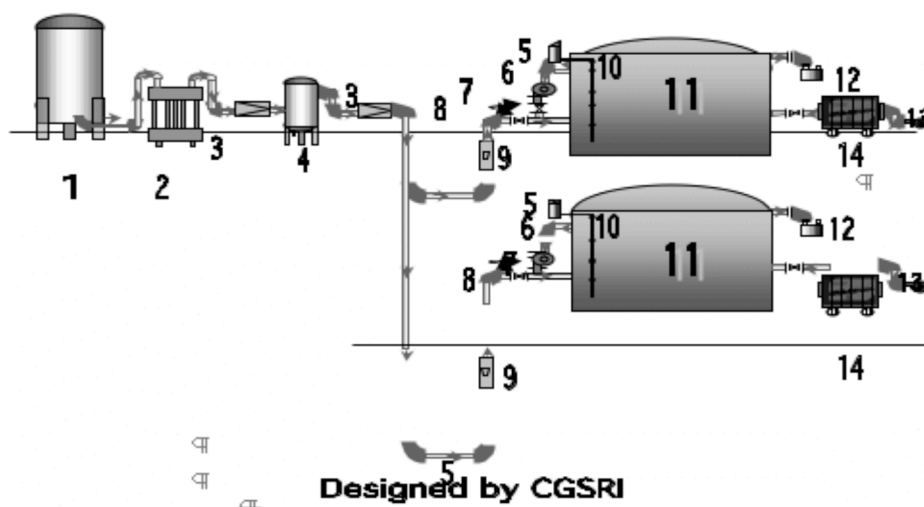


Figure 1. Technical flow chart of CO₂ storage of grain designed by Chengdu Grain Storage Research Institute (CGSRI).

- 1. CO₂ cylinder, 2. evaporator, 3. decomposition facility, 4. gas balance cylinder, 5. CO₂ supply pipeline, 6. circulation pipeline, 7. circulation fan, 8. switch valve, 9. flow meter, 10. auto-monitor system for CO₂ concentration, 11. warehouse storage with CO₂, 12. pressure balance facility, 13. fan, 14. intelligent control system

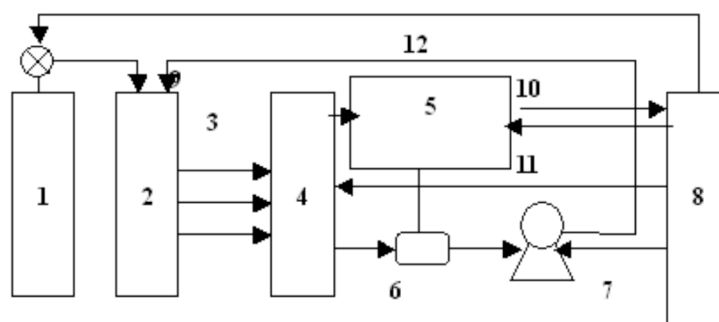


Figure 2 - The principle of automatic system for monitoring CO₂ concentration.

- 1. CO₂ supply source, 2. warehouse storage with CO₂, 3. sampling from multiple lines, 4. multicenter control device, 5. infrared CO₂ detect facility, 6. buffer, 7. pump, 8. inspection computer for telecontrol, 9.CO₂ supply control device, 10.data output, 11.on-off control 12 signal return

Auto-monitor system for CO₂ concentration

The system consists of a gas sampling pipe network, gas control pipeline, infrared CO₂ detector facility, data traffic device, CO₂ supply control device, inspection computer, inspection software, that are shown in Fig. 2.

The system can determine and report the CO₂ concentration of several points in the warehouse automatically, and can be run on MS Windows as well as being user friendly to operate and update. Due to its excellent performance, the CO₂ concentration could be reliably recorded on-line, thus also lead to utilizing the CO₂ resource reasonably effectively and economically. The system was based on the detection standard of China Measurement Technology Institute. The detection limit was 0-100%, basic error $\leq 1.0\%$, F·S., repeatability $\leq 0.5\%$ F·S, drift of zero and span $< 1.0\%$ F·S/48h).

Safety and Security Facilities

To prevent pressure differences from occurring between inside the warehouse and the ambient, two sets of pressure balance facilities were assembled in each bin. The pressure could be detected up to a level of $\pm 2,000$ Pa with a precision of ± 20 Pa. In addition four sets of oxygen-breathing devices were provided as a standard safety regulation during operation.

APPLICATION OF CO₂

After the first-period construction had been accomplished, field experiments were carried out for one year. During the first period of CO₂ storage, the CO₂ concentration ranged from 70% to 35% maintained for more than 14 days, while during the second period, a continuous effective concentration of CO₂ was maintained.

Effect on Insects

Materials and Methods

Test Insects: Two weeks old, adult insects of strains of *Sitophilus zeamais*, *Rhyzopertha dominica* and *Tribolium castaneum* resistant and susceptible to phosphine of were tested. The resistance factors were 196, 204 and 8 respectively. Each test contained 20 adults and mixed-stage insects (eggs, larvae, pupae) of each of the above test insects. A control test was prepared in the same way but was placed in the conventional storage. Each test was done in 10 replicates. After 1 month exposure, the mortality rate was recorded, and all the insects were sieved out and the grain samples were kept in an incubator at $25 \pm 1^\circ\text{C}$, $70 \pm 5\%$ r.h.; and at $30 \pm 1^\circ\text{C}$, $70 \pm 5\%$ r.h. to count the number of the next progeny. The emergence of the progeny was observed 56d after treatment.

Treatment of the test insects: The test groups numbered 1~6 were laid at the four corners of the warehouse at different heights. The test groups numbered 7~10 were laid at the vent openings and check doors.

Results

Tests in the wheat warehouse storage under CO₂. All test adults of the of two strains of the three insects species were totally controlled. No next progenies of the mixed-stage cultured insects emerged after 56 days treatment.

Tests in the paddy warehouse storage under CO₂: All test adults of the of two strains of the three insects species were totally controlled. No next progenies of the mixed-stage cultured insects emerged after 56 days treatment.

The insects that originally existed in the warehouse before treatment: It was found that the insect density of samples from No. 13 wheat warehouse under CO₂, was about 15 insects/kg wheat, consisting mainly of *S. zeamais* and *Sitotroga. cerealella*. After the treatment with controlled CO₂, no insects emerged over the next half year. The same situation was found in samples from No. 14 wheat warehouse under CO₂, which were infested with Psocidae (booklice) before treatment, while after treatment no live booklice were found in the warehouse.

Conclusions

The results clearly demonstrated that the treatment of 70% - 35% CO₂ for 14 days was very effective against each stage of the tested insects (susceptible and resistant), and no residual live insect populations remained in the grain.

These trials showed also that the application of controlled CO₂ was effective against psocids, which could be an alternative control method for this insect family.

Effect of CO₂ on Molds

Materials and Methods

Warehouses: Bins Nos. 12, 13, 14 and 15 were chosen as test for CO₂ storage, each bin contained 3,000 - 5,000 tonnes of grain;

Test Grain: Newly-harvested paddy and wheat from Sichuan and Hunan, with moisture content of 11.6% -12.3%;

Sampling: Grains were sampled every 3 or 4 months over a one year period for analysis of mycoflora in the grain. The preparation of samples was conducted by the Chinese standard method GB4789-1-94.

Results

Through the 370 days of CO₂ grain storage in the field trials, the results of grain fungal colonies can be seen in Table 1. Test results of bacterial counts were omitted from this table.

TABLE 1

Result of colonies of fungi recorded on grain stored under CO₂ and on grain stored under normal atmospheric conditions (unit: colony formation units (CFU) per gram grain).

Warehouse number and type	Grain storage category	Initial CFU	After 185 days CFU	After 370 days CFU
No.10 normal warehouse	Paddy	5.4x10 ³		2.5x10 ³
No.11 normal warehouse	Wheat	5.6x10 ²	8.95x10 ³	1.5x10 ³
No.12 CA warehouse	Paddy	2.7x10 ⁴		2.5x10 ³
No.13 CA warehouse	Wheat	3.7x10 ²	8.5x10 ²	4.7x10 ³
No.14 CA warehouse	Wheat	7.8x10 ²	8.2x10 ²	1.9x10 ³
No.15 CA warehouse	Wheat	6.1x10 ²		5.7x10 ²

Discussion

Examination of data on the number of fungal colonies of the wheat and paddy stored under CO₂ revealed that a slight change occurred over the one year of storage period. But when we examine and analyze the bacterial population, the results did not differ between the initial counts and after one year of storage under CO₂. Because of limited access to sampling ports of the storage under CA, only small samples could be taken. But the field fungi which can reflect grain freshness degree hypnocyist and Fusarium avenaceum were reduced gradually. Though the test-out rate which is represented by the Aspergillus glaucus, Aspergillus flavus, Aspergillus candidus is high, it was stable on the whole. The tested fungal categories, at suitable moisture content and with the extension of storage time are capable of reducing the grain quality. However, by applying the CO₂ storage, development of fungi at the tested moistures was not apparent.

Effects of CO₂ treatment on grain quality

Materials and methods

Experimental: Warehouses No. 12 containing paddy, No. 13 and No. 14 containing wheat were chosen for CO₂ treatment and two untreated warehouses No. 10 containing paddy and # 11 containing wheat were selected as controls. In contrast to the CO₂ treated grain, the controls were fumigated using PH₃ by recirculation to control the insect pests. Samples were taken for testing grain quality before the trial, in October and in April and May of the following year.

Test for quality parameters: Test methods for long-grain non-glutinous rice and wheat quality were according to the international standards. For moisture content, fatty acid, and degree of conglutination, the samples were tested at 105°C constant weight method of GB5497-85, the cereal fatty acid measurement method of GB/T15684-1995 and the capillary movement conglutination degree measurement method of GB5516-85 respectively.

Quality index: The quality index used in this trial was based on long-grain non-glutinous rice and wheat storage of "The quality judgment standards of grain and oil storage" used by the National Grain Reservation Bureau and the National Quality Technology Supervision Bureau in 1999, as well as according to the grain classing standards of "Paddy" of the international standards GB1350-1999 and "Wheat" of the GB1351-1999 to classify grains.

Results

Effects on quality of long-grain non-glutinous rice: The experimental results are shown in Table 2.

Table 2 shows that after 10 months storage the regress scoring value of CO₂ treated storage and normal storage decreased by 8.8 fen and 11.4 fen, respectively. The acid value of CO₂ CA storage and normal storage increased by 2.1 KOH mg/100g dry-sample and 4.8 KOH mg/100g dry-sample, respectively.

The acidity of CO₂ CA storage and normal storage rises to 0.3 KOH mg/10g, dry-sample and 0.4 KOH mg/10g dry-sample, respectively. The conglutination degrees of CO₂ CA storage and normal storage were reduced by 3.7mm²/s and 4.2mm²/s, respectively. Germination rate of CO₂ CA storage and normal storage decreased by 28% and 43%, respectively. These results indicate that CO₂ CA storage significantly

slows quality changes compared to normal storage. For extended storage time, it is assessed that the advantage of CO₂ CA storage will be further revealed especially under hot and wet adverse climatic conditions.

TABLE 2

Effects of CO₂ treatment on long-grain non-glutinous rice quality compared to untreated grain; tests were based on samples taken from the experimental facilities.

	Date	Storage quality controlling index of long-grain non-glutinous rice						Acidity Hml/10g sample	Quality index							
		Fatty acid value KOH g/100g dry sample	Degree of viscosity (mm ² /s)	Germination percentage %	Regret value	Tasting value (fen)	Color scent		Broken rice %	Whole grain %	Impurity %	Moisture %	Insoluble matter %	Outside matter %	Yellow rice %	Comprehensive evaluation
No.12 CA warehouse	2002.5.20	19.7	14.6	80	96.2	81	normal	1.0	76.9	54.0	0.7	12.7	5.6	1.4	0	Third class
	2002.10.25	20.9	12.3	63	90.8	79	normal	1.2	76.7	54.3	0.8	12.7	5.9	1.3	0	Third class
	2003.4.8	21.8	10.9	52	87.4	78	normal	1.3	77.0	54.0	0.8	12.7	7.1	1.0	0.3	Third class
No.10 normal warehouse	2002.5.20	19.1	14.8	77	96.5	81	normal	1.1	76.8	53.6	0.7	12.3	6.8	1.1	0.6	Third class
	2002.10.25	22.4	12.3	41	88.9	79	normal	1.3	76.2	55.4	0.4	12.5	8.1	0.3	0.2	Third class
	2003.3.15	23.9	10.6	34	85.1	78	normal	1.5	76.1	53.0	0.6	12.6	8.3	0.6	0.3	Third class

Effects on wheat quality: The experimental results are shown in Table 3.

TABLE 3

Effects of CO₂ treatment on wheat quality compared to untreated grain; tests were based on samples taken from the experimental facilities.

Number of Warehouse	Sampling time	Storage quality controlling index of wheat				Quality index of wheat				
		Degree of viscosity (mm ² /s)	Flour water absorption (%)	Taste value (fen)	Color scent	Bulk density g/L	Unsound kernel %	Impurity %	moisture %	Comprehensive value
No.13 CA warehouse	2002.5.21	7.0	197	75	normal	775	6.4	0.6	11.9	Second class
	2002.10.18	8.2	197	77	normal	778	8.0	0.5	12.0	Second class
	2003.4.7	8.1	201	77	normal	778	6.4	0.7	12.1	Second class
No.14 CA warehouse	2002.5.22	7.4	196	75	normal	769	5.8	0.7	11.6	Third class
	2002.10.18	7.6	200	77	normal	769	9.7	0.7	11.9	Third class
	2003.3.17	7.7	212	77	normal	772	8.7	0.7	12.1	Second class
No.11 CA warehouse	2002.5.21	8.2	187	75	normal	770	10.4	0.8	11.8	Second class
	2002.10.21	9.3	194	77	normal	775	9.8	0.7	12.2	Second class
	2003.3.16	8.3	206	77	normal	781	10.8	0.7	12.1	Second class

Table 3 shows that after 10 months, wheat quality had some improvement under CO₂ storage. This quality improvement may be associated with the physiological late maturity of wheat. Because of the improved wheat storage conditions, an additional advantage of CO₂ storage over normal storage could be in its capacity to enable long term storage.

Effect of CO₂ treatment on grain quality after unsealing

Experimental method

After 50 days of unsealing, tests were carried out on long-grain non-glutinous rice samples taken from No.12 CA facility. Samples were taken every 10 days for determination of moisture content, fatty acid, acidity, conglutination degree, germination rate, taste value, color and aroma. During the same period tests were also carried out for broken rice yield and wholesomeness.

Results

The experimental results are shown in Table 4.

TABLE 4
Effects of CO₂ treatment on long-grain non-glutinous rice quality of samples taken from storage in No.12 facility after unsealing.

Days after unsealing	Storage quality controlling index of rice							Quality index of rice							Comprehensive value
	Fatty acid value KOHmg/100g dry-sample	Degree of viscosity (mm ² /s)	Germination percentage %	Regret value	Taste value (fen)	Color	Acidity KOHml/10g sample	Broken rice yield %	Wholesomeness %	Unsound kernel %	Moisture content %	Unsound kernel %	Outside of paddy %	Yellow rice %	
0	21.8	10.9	52	87.4	78	normal	1.3	77.0	54.0	0.8	12.7	7.1	1.0	0.3	Third class
10	22.3	11.1	51	87.6	78	normal	1.3				12.7				
20	22.6	10.4	50	86.3	78	normal	1.3				12.7				
30	22.6	10.3	52	86.2	78	normal	1.3				12.7				
40	22.6	10.3	52	86.2	78	normal	1.4				12.7				
50	22.6	10.3	52	86.2	78	normal	1.3	76.9	53.6	0.8	12.7	6.6	0.9	0.3	Third class

Table 4 shows that after unsealing, the quality controlling index and quality index had not markedly changed. This suggests that safe moisture, good-quality grain

stored under CO₂ will not be adversely changed after unsealing.

Economic benefit analysis

Experimental conditions and approaches

The economic analysis was carried out on warehouse No.12 for paddy stored under CA, and warehouse No.13 for wheat stored under CA. Warehouse No.10 for paddy and No.11 for wheat were stored under normal conditions, served for comparison and were synchronously constructed, to record the storage expenses. Comparative analysis of expense of direct materials (CO₂ and PH₃), auxiliary materials, water and electricity consumed, maintenance, and the character of environment protection, and expected benefit was carried out after one year.

Results

Results of economic analysis are shown in Table 5.

TABLE 5
Economic analysis that compares CA treatment compared to normal storage in warehouse
(unit: yuan)

Number of warehouse	No.10 normal warehouse	No.11 normal warehouse	No.12 CA warehouse	No.13 CA warehouse
Grain storage variety	Paddy	Wheat	Paddy	Wheat
Direct material cost in press-house period	0.79	0.58	2.49	1.94
Direct material cost in normal storage period	0.54	0.36	1.70	1.30
Usage cost in normal storage period per ton	1.87	1.31	2.95	2.25
Newly increased benefits beforehand per ton in a year	0	0	47.05	47.75

Notes: 1. Statistics compare expenses of the two grain-storages without administrative expenses.

2. Expected benefit is based on normal grain storage criteria. If CA grain storage is extended to two years, storage per half a kilogram evaluate 0.05 yuan, then the income will rise to 50 yuan per year: 50 yuan/t*year

Analysis

Expenses of CO₂ grain storage per tonne in a year for paddy and wheat are less than 3.0 yuan, 2.5 yuan respectively. If we adopt atmosphere source which are in line with the food-class liquid CO₂ standards (GB10621-89) of China, then the price will be reduced from 960 yuan per tonne at present, to 600 yuan, and the usage expense of paddy and wheat will be under 2.3 yuan, 1.8 yuan per tonne/year respectively. Direct materials costs will also be under 1.0 yuan per tonne/year.

CA grain storage under CO₂ is characteristically termed as “green-grain” storage. The grain having been stored for two years with CA storage, after being offered into

the market, prices are expected to increase above 40 yuan per tonne in a year according to the principle that superior quality should have higher price.

CA grain storage can kill pests effectively, prohibit bacterial development, prolong the storage period, and avoid chemical toxicity to humans, contamination of the grain and the environment. Furthermore, it can avoid rapid build-up resistance to pesticides which is a factor whose benefit is difficult to estimate. It answers the demand for “green-food” and the current demand of the foodstuff market. These hidden social and economic benefits can not be directly translated into monetary gain, so their comprehensive economic benefit is higher than the normal grain storage practice.

Demonstration effect and prospect

The success in the construction of the model facility under CO₂ CA grain storage and the results achieved in the field suggest the following:

- * To rebuild properly the tall bungalow warehouses which are commonly constructed at present in the P..R.China, and then ensure that the gas tightness can hold a 500Pa pressure half life of 12 minutes. Such levels of gas tightness should fulfill the requirement for the application of the CA storage technology.
- * The technology and the equipment used in the P.R.China can completely provide the centralized gas supply system used presently, and automatically monitor CO₂ concentrations inside the warehouse.
- * CA techniques can effectively prevent and control grain storage pests and completely avoid using pesticides thereby preventing pollution of the environment and enabling green-storage of commodities.
- * The use of CA storage under CO₂ inhibits the development of saprophytic microflora on foodstuffs without change in quality.
- * By storage under CO₂ for 10 months, long-grain non glutinous rice quality is superior to that under the normal storage. Because of the delayed ripeness and endurance of wheat, this effect on wheat is not significant. Removal of the seal will not adversely affect the quality of grain stored under CO₂.
- * Storage under CO₂ has economic and social benefits that exceed normal storage and is in line with the trend for the demand of “green food” in the grain market.

Prospects

The CO₂ storage technology is feasible for construction and application as an advanced technology of green storage under P.R.China conditions.

- The successful realization of the five large CA experimental grain facilities in the P.R.China in 2002 further suggests that the time is ripe for the popularity and potential application of this technology in the country.
- This technology is appropriate for diversification efforts aimed at achieving high quality, high benefit, high nutrition value, low loss rates, low pollution and reduction in cost of operations. The technology is likely to further expand and popularize with the economic development and expanding grain marketing system.

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