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Evaluation of Large, Modern Warehouse Storages Designed and Constructed for Application of Carbon Dioxide

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Abstract: The updated warehouses of controlled CO_2 storage with total capacity of 45 000 t were constructed at Mianyang, in which field experiments were successfully carried out. This paper introducs the construction techniques, CO_2 supply and distribute system, auto-monitor system, security and guarantee facilities, sealing materials, airtight techniques and field experiments by the techniques of CA grain storage couplied with natural low temperature grain storage. The results showed that design and construction techniques were reasonable. The pressure decay half-life reached 12 min from 500 pa declined to 250 Pa, and thus effectively ensured the concentration of CO_2. Auto supply and distribution for CO_2 as well as monitoring were realized during the whole process. The field experiment proved that both susceptible strains and resistant strains of *Sitophilus zeamais*, *Rhizopertha dominica* and *Tribolium castanuem* were 100% controlled with exposure for more than 14 d to CO_2 which concentration ranged from 35% – 75%. After incubating the mixed samples at different culture-conditions for 42 d, no alive adults appeared. There were also no significant changes in the quantity of carried microorganism in the grain stored with CO_2. Compared with conventional storage, after 40 months storage with CA grain storage couplied with natural low temperature grain storage for the new-harvest grain with safe moisture content and good quality, the grain quality was better and could be steady after unsealing.

Key words: CO_2 CA storage, natural low temperature grain storage, grain depot construction, field experiments

Introduction

With the continuous progress of technology and advance of life quality, people care much about the environment, and require of "green food", which are of high quality with no-chemical contamination. Current grain storage technology is developing towards an integrated way to reducing use of chemical pesticides, which including low-temperature storage, controlled atmosphere (CA) techniques and biological techniques. The controlled CO_2 techniques means inflating CO_2 into well-sealed warehouse so as to change the ecological storage environment, inhibite molds and respiration of grain, control pests, and delay grain aging.

Since 2000, the first modern warehouses with controlled CO_2 were constructed at Mianyang, China, with a total capacity of 45 000 t and consist of several chambers with a capacity of more than 5000 t for each. After the first-period construction, experiments were carried out compared with conventional storage.

1 Construction of the CA Warehouses

1.1 Construction Techniques

1.1.1 Condition of the warehouses

Warehouses with Controlled CO_2: 5 horizontal warehouses consist of 2 chambers, 24m width 96m length × 7.8m height, 6m height of grain bulk, 45 000 tons of total capacity, 5 000 tons capacity of each chamber.

Control Warehouses 1 horizontal warehouse with the same condition of the above, which adopts conventional storage as control.

1.1.2 Sealing Material

Based on the requirements of controlled CO_2 warehouse, several materials were screened out by comparation, which were flexible, tractile, resistant to extreme temperature and erosion, ultra-radiation-proof, non-contaminant or non-toxic, durable, easy to use, of low air-permeability, good adhesive ability, and with reasonable price.

1.1.3 The Position and Methods for

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Sealing

According to the original design, the following steps were conducted:

Equipped the windows and venting pipes with air-tight and heat – preservation facilities as well as axial-flow fans to the windows →

Brushed the interior wall of the warehouse with Coating A ↓

Sealing the wall, top, and floor of warehouse, made each bonding point into arch camber of 150 mm thickness ↓

Filled high elastic materials into the gaps of the camber ←

Sealed all the openings of the warehouse, including the inlet hole, outlet hole, vent opening, axial-flow opening, check opening, CO_2 supply opening, and bonding point of lines etc.

1.1.4 Air-tightness of the Warehouses with CO_2

The pressure decay half-life of the warehouse with CO_2 reached more than 12 min from 500 pa declined to 250 pa, while the control only reached nearly 40 s. Through inspection, it was proved that the concentration of CO_2 could be effectively ensured by one-time introduction of CO_2.

1.2 Assembly of Assorted Facilities for Warehouses with CO_2

The key point for CO_2 storage techniques was assembling assorted equipments. In the construction, large-scale CO_2 supply and distribute system was conducted at the first time, which realized central supplying and distribution of CO_2. At the same time, auto-monitor system and security and guarantee facilities for CO_2 were developed and applied. Figure 1 shows the technical flow chart:

1.2.1 CO_2 supply and distribute system

The CO_2 supply and distribute system is used to store liquid CO_2 safely, vaporize and send gas CO_2 when necessary.

1.2.2 Auto-monitor system for CO_2 concentration

The system consist of gas sampling pipe network, gas control pipeline, infrared CO_2 detection facility, data traffic device, CO_2 supply control device, inspection computer, inspection software, which are shown in figure 2.

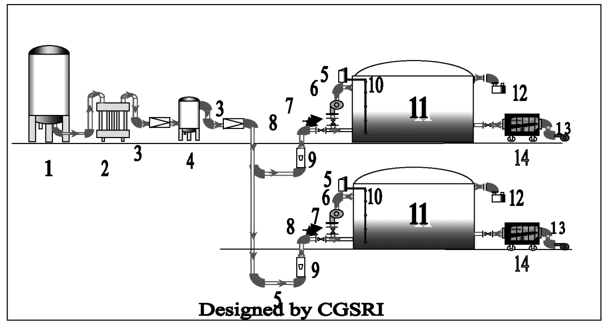

Fig. 1 Technical flow chart of CO_2 storage of grain designed by Chengdu Grain Storage Research Institute (CSR)

1. CO_2 cylinder, 2. evaporator, 3. decompression facility, 4. gas balance cylinder, 5. CO_2 supply pipeline, 6. circulation pipeline, 7. circulation fan, 8. switch valve, 9. flow meter, 10. auto-monitor system for CO_2 concentration, 11. warehouse storage with CO_2, 12. pressure balance facility, 13. fan, 14. intelligent control system

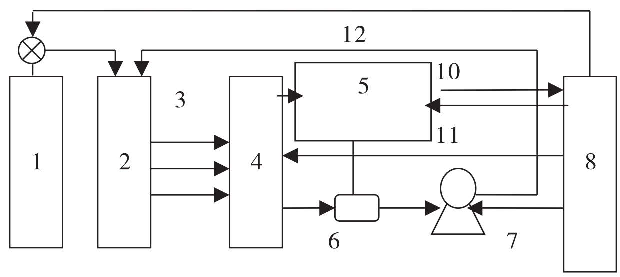

Fig. 2 The principle of auto-monitor system for CO_2 concentration

1. CO_2 supply source, 2. warehouse storage with CO_2, 3. sampling from multiple lines, 4. multicenter control device, 5. infrared CO_2 detect facility, 6. buffer, 7. pump, 8. inspection computer for telecontrol, 9. CO_2 supply control device, 10. data output, 11. on-off control, 12. signal return

The system could determine and report the CO_2 concentration of several points in the warehouse automatically, and can be run on MS Windows as well as be friendly for user to operate and update. Due to its excellent performance, the CO_2 concentration could be detected on-line well and truly, thus also lead to utilizing the CO_2 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 ≤1.0% (F · S), repeatability ≤ 0.5% (F · S); drift of zero and span < 1.0% (F · S)/48h.

1.2.3 Security and Guarantee Facilities

In order to avoid the troubles due to pressure difference between inside-warehouse and out-side warehouse, 2 sets of pressure balance facilities were assembled with each chamber of the warehouse. The adjust scope for pressure ranged from 2 000Pa with detect precision of 20Pa. At the same time, 4 set of tote oxygen – breath devices were equipped and a relevant standard regulation was established, which all ensured the safety during operation.

2 The Application of Grain Storage with CO_2

After accomplished the first-period construction, field experiments were carried out for one year. During the first period of CO_2 storage, the CO_2 concentration ranged from 70% to 35% maintained more than 14day, while during the second period, effective concentration of CO_2 was maintained.

2.1 Effect Against the Insect Pests

2.1.1 Materials and Methods

Test Insects: Susceptible and resistant strains to phosphine of two weeks adult insects of *S. zeamais*, *R. dominica* and *T. castanuem* were tested. The resistant factors were 196, 204 and 8. Each test contains 20 adults and mixed-stage insects (eggs, larvae, pupae) of each above test insects. Control test was prepared the same way except adopt 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 kept in incubator of 25(1 ± ℃, 70% ± 5%; 30 ± 1℃, 70% ± 5% respectively to count the number of the next progeny. The emergence of progenies was observed 56d later after treatment.

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

2.1.2 Results and Analysis

2.1.2.1 The Results of Test in Wheat Warehouse Storage with CO_2: All test adults of 3 insects of 2 strains were 100% killed. No next progenies of the mixed-stage cultured insects emerged after 56 days treatment.

2.1.2.2 The Results of Test in Paddy Warehouse Storage with CO_2: All test adults of 3 insects of 2 strains were 100% killed. No next progenies of the mixed-stage cultured insects emerged after 56 days treatment.

2.1.2.3 The Original Insects Existed in the Warehouse Before Treatment: It was found that the insect density of NO. 13 wheat warehouse with CO_2, was about 15 insects/kg wheat, which mainly consist of *S. zeamais* and *S. cerealella*. While after treatment with controlled CO_2, there were no insects emerging in the next half year. The same condition was with the NO. 14 wheat warehouse with CO_2, which had found booklice before while after treatment no booklice was alive in the warehouse.

2.1.3 Conclusion

From the result, it was clear that the treatment of 70% – 35% CO_2 for 14 days was very effective against each stage of the tested insects (susceptible and resistant). And no residue will be lead to at the same time.

The field experiment also showed that the techniques of controlled CO_2 was effective against booklice, which could be an alternative for control of booklice.

2.2 Inhibition Effect Against Molds

2.2.1 Materials and Methods

Warehouses and Test Grain

Warehouses: The new warehouse No. 12, 13, 14 and 15 were chosen as the test warehouses for CO_2 storage, each test warehouse contained with 3 000 – 5 000 t of grain;

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

Sampling: Sampled every 3 or 4 months to analysis mycoflora in the grain, which had been stored for 1 year. The preparation of samples was conducted by the Chinese standard method GB4789 – 1 – 94.

2.2.2 Experimental Result and Analysis

2.2.2.1 Result

Through 370 days' CO_2 CA grain storage in the field, the examination result of grain fungi's germ quantity can be seen from the table 1, the examination of bacteriallogzaph is omitted.

Table 1. Examination result of grain fungi's germ quantity of the grain stored by CO_2 CA storage and by the normal storage of the exemplary facility (unit: entry per gram)

Warehouse number and type	Grain storage category	First	185 days	370 days
No. 10 normal warehouse	Paddy	5.4 × 103		2.5 × 103
No. 11 normal warehouse	Wheat	5.6 × 102	8.95 × 103	1.5 × 103
No. 12 CA warehouse	Paddy	2.7 × 104		2.5 × 103
No. 13 CA warehouse	Wheat	3.7 × 102	8.5 × 102	4.7 × 103

Warehouse number and type	Grain storage category	First	185 days	370 days
No. 14 CA warehouse	Wheat	7.8 × 102	8.2 × 102	1.9 × 103
No. 15 CA warehouse	Wheat	6.1 × 102		5.7 × 102

2.2.2.2 Analysis

We can see from the examination datum in the field germ quantity and bacteriallogzaph: grain fungi's germ quantity of the wheat and paddy which are stored by CO_2 CA in one year changes a little during the whole storage period. But when we examine and analyze the grain mildew bacteriallogzaph, the result has no obvious variety. Because of being limited by CA sampling, we take little specimen . But general speaking being handled by CO_2, the field fungi representative which can reflect grain's freshness degree—*hypnocyst* and *Fusarium avenaceum* are reducing gradually. Though the test-out rate which is represented by the *Aspergillus glaucus link*、*Aspergillus flavous link*、*Aspergillus candidus link* and so on is high, it was stable on the whole. The test-out fungi categories reduce gradually with the extension of storage time. Therefore adopting the CO_2 CA storage grain fungi are regardless on the quantity and the category for the complete moisture grain.

2.3 Quality Influent Effect

2.3.1 Experimental Material and Method

2.3.1.1 Experimental method

Choose there CA warehouses (No. 12 paddy warehouse, No. 13 wheat warehouse) which are newly set up by exemplary facility and two normal warehouses which are set up synchronically (No. 10 paddy warehouse and No. 11 wheat warehouse) as experimental warehouse. Conduct grain storage contrastive experiment of CO_2 CA and normal storage (mostly points PH_3 recirculation fumigation to kill pests). Measure grain's quality before this experiment, in October continuously and in May and April of the second year.

2.3.1.2 The method of quality judgment

The method of long-grain nonglutinous rice and wheat 's quality judgment is in line with the international standards. The moisture, the value of fatty acid and the conglutination degree were judged by the 105 ℃ constant weight method of GB5497 – 85, the cereal fatty acid measurement method of GB/T15684 – 1995 and capillary movement conglutination degree measurement method of GB5516 – 85.

2.3.1.3 The method of quality judgment

The quality index measured by this experiment is on the basis of the long-grain nonglutinous rice and wheat's storage quality controlling index of "The quality judgment standards of grain and oil storage" (try out), unitedly distributed 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 class grain.

2.3.2 Experimental result and analysis

2.3.2.1 The quality effect of long-grain nonglutinous rice

The experimental result can be seen from table 2.

Table 2. The long – grain nonglutinous rice's quality measurement result of CO_2 CA grain storage and the normal grain storage of the exemplary facility

Samping time (year. month)	Fatty acid value KOHmg/100g dry samle		Degree of viscosity mm^2/s		Germination percentage %		Tasting valuation score		Color & scent	
	No. 12	No. 10	No. 12	No. 10	No. 12	No. 10	No. 12	No. 10	No. 12	No. 10
2002.04	21.9	21.1	13.5	16.0	77	70	81	82	normal	normal
2002.09	20.2	21.6	13.5	16.0	65	68	–	80	normal	normal
2003.03	21.6	22.7	9.0	9.4	52	16	77	73	normal	normal
2003.09	22.4	26.1	8.8	8.8	41	17	77	73	normal	normal
2004.03	24.5	27.0	8.6	9.1	41	3	77	73	normal	normal
2004.09	26.4	32.0	8.6	–	24	–	–	77	normal	normal
2005.03	27.8	worked off	–	worked off	–	worked off	75	worked off	normal	worked off
2005.09	27.3	worked off	–	worked off	–	worked off	75	worked off	normal	worked off

No. 10: normal warehouse; No. 12: CA warehouse; – : no determine;

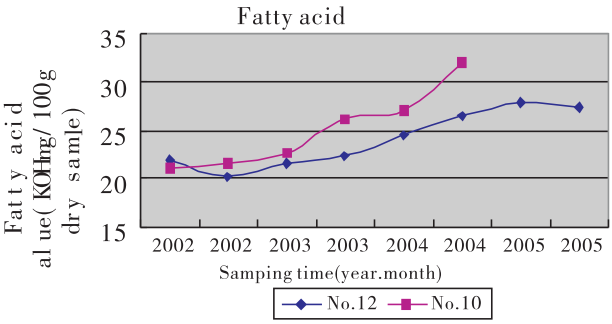

Fig. 3 **The changes of Fatty acid value way and normal way**

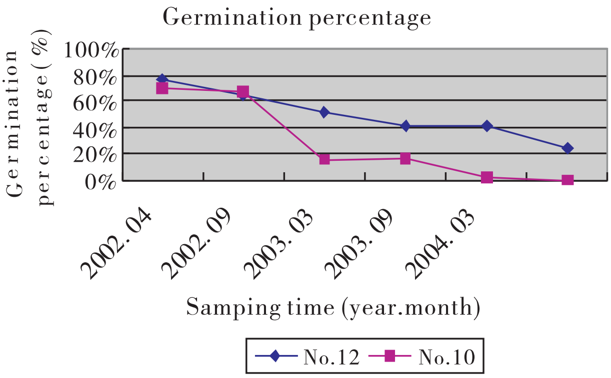

Fig. 4 **The changes of Germination percentage stored by CA stored by CA way and normal way**

We can see from the table 2, fig. 3 and fig. 4: After 40 months storage with CA storage coupling with natural low temperature storage for the long-grain nonglutinous rice with safe moisture content and good quality, the grain quality stored by CA was better than that of stored by normal grain storage. And it also explains that CO_2 CA storage changes slowly than normal storage. If reserved continuously the difference between them will enlarge and the advantage of CO_2 CA storage will be revealed further especially under high-hot and high-wet abominable circumstance.

2.3.2.2 Wheat's quality effect

Table 3 suggests the experimental result:

Table 3. **Wheat's quality tested result of CO_2 CA grain storage and the normal grain storage of the exemplary facility**

Samping time	Degree of viscosity mm^2/s		Flour muscle absorption%		Tasting valuation fen	
	No. 11	No. 13	No. 11	No. 13	No. 11	No. 13
2002.05	8.2	7.0	187	197	75	75
2002.10	9.3	8.2	194	197	77	77
2003.04	8.3	8.1	206	201	77	77
2004.04	8.1	8.1	202	204	74	74

No. 11: normal warehouse; No. 13: CA warehouse;

We can see from table 3: After 24 months wheat's quality has some improvement with CO_2 CA storage and normal storage. Furthermore, the difference between them is not obvious. Wheat's physiological late maturity and technologic late maturity give rise to wheat's quality improvement. Because wheat's capacity of bearing storage is good, the advantage of CO_2 CA storage over normal storage require a long time to reveal.

2.4 Quality Variety of CO_2 CA Storage after Unsealing

During the very day when they are unsealed to 50 days after disclosing, measure periodicallylong-grain nonglutinous rice's variety of CO_2 CA storage in No. 12 CA facility, which was taken sample every 10 days to moisture content, fatty acid, acidity, conglutination degree, sprouting rate, tasting value, color scent and scent. During the same period measure Broken rice yield and whole releas and analyze speed of the quality variety.

Experimental result can be seen from table 4

Table 4. **Long-grain nonglutinous rice's quality variety of CO_2 CA storage in No.** 12 **facility after unsealing**

Days of unsealing	Storage quality controlling index of wheat						acidity KOHmL/10g sampler
	Fatty acid value KOHmg/100g dry-sample	Degree of viscosity mm^2/s	Germination percentage %	Regress value	Tasting valuation score	Color & scent	
0	21.8	10.9	52	87.4	78	normal	1.3
10	22.3	11.1	51	87.6	78	normal	1.3
20	22.6	10.4	50	86.3	78	normal	1.3
30	22.6	10.3	52	86.2	78	normal	1.3
40	22.6	10.3	52	86.2	78	normal	1.4
50	22.6	10.3	52	86.2	78	normal	1.3

We can see from table 4: After unsealing quality index has no obvious change, and storage quality controlling index changes slowly. It suggests that safe-moisture, good-quality grain which is dealt with rational CO_2 CA storage technology will not be badly changed after unsealing.

2.5 Experimental Result and Analysis

We can make conclusion from the above datum analysis:

2.5.1 Experimental Result

2.5.2 The usage expense of CO_2 CA grain storage per ton in a year is that 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 CO_2 standards (GB10621 – 89) of our country, then the price will reduce from 960 yuan per ton at present to 600 yuan, the usage expense of paddy and wheat will be under 2.3 yuan, 1.8 yuan per ton in a year respectively, direct materials cost also will be under 1.0 yuan per ton in a year.

2.5.3 CO_2 CA grain storage is character of green grain storage. The grain being stored for two years with CA storage after being plunged into the market expects to increase above 40 yuan per ton in a year according to the principle that superior quality should has higher price.

2.5.4 CA grain storage can kill pests effectively, prohibit bacteria, prolong grain storage's change worse rapidly, avoid chemical's danger for human, grain and environment. It can't erode the relevant establishment of grain warehouse and endanger PH_3 materials in PH_3 fumigation. Furthermore, it can avoid factor which can't be exactly numerated like the strength of grain storage pests' fastness. It answers for the demand of green food and current of foodstuff market. This latent social and economic benefit can't directly be accounted by money, so its comprehensive benefit, economic benefit is higher than that of normal grain storage pattern.

3 Demonstration Effect and Prospect

3.1 Demonstration Effect

Succeeding in construction of exemplary facility with CO_2 CA grain storage and applying in the field suggest:

3.1.1 Rebuild properly the tall bungalow warehouses which is constructed in our country at present, then the warehouse's air-tightness can attain 500 Pa pressure half life 12 min, which can entirely fulfill the demand of CO_2 CA grain storage technology for the warehouse's air-tightness.

3.1.2 Our country's technique and equipment can completely realize the mode of centralized air feed at present and automatic supervise function of CO_2 concentration inside of the warehouse.

3.1.3 Reasonable C. A techniques can effectively prevent and control grain storage pests and completely avoid using chemistry medicament. Therefore, no social effects of pollution and no pollution green-storage will come true.

3.1.4 If we use CO_2 CA storage, then the foodstuff epiphyte will have no evident change not only quantity but also species for complete moisture foodstuff.

3.1.5 With CO_2 CA storage in 10 month, long-grain no glutinous rice's quality is superior to that of the normal storage. The wheat's contrastive effect is not obvious, because of its late ripeness and endurance. The quality of grain which is reserved rationally with CO_2 CA techniques will not become bad swiftly after unsealing.

3.1.6 If we use CO_2 CA storage, the grain storage comprehensive economic benefit and social benefit will excel to normal storage and it's developing direction will accord with the trend of the demand of green food and grain market.

3.2 Prospect

3.2.1 CO_2 CA storage technology is feasible for our construction and application as a sort of advanced technology of green storage.

3.2.2 The success that four CO_2 CA enlargement experimental grain facilities have constructed in China in 2002 further suggests the popularity and application of this technology in our country have been mature.

3.2.3 This technology is suited for the direction of diversification, high quality, high benefit, high nutrition, low waste, low pollution and low cost. It will further enlarge and popularize with the consummation of our country's economic development and grain's market system.

References

[1] Annis, P. C., and van Someren Greve, J. (1984b). The use of carbon dioxide for quality preservation in small sheeted bag stacks, in Controlled Atmosphere and Fumigation in Grain Storages

[2] Banks, H. J., and Annis, P. C. (1980b). Con-

version of Existing Grain Storage Structures for Modified Atmosphere use. In ' Controlled Atmosphere Storage of Grains'

[3] Banks, H. J., Annis, P. C., Henning, R. C., and Wilson, A. D. (1980a). Experimental and Commercial Modified Atmosphere Treatments of Stored Grain in Australia. ' In Controlled Atmosphere Storage of Grains'

[4] H. J. Banks and B. E. Ripp. Sealing of Grain Storages for Use with Fumigants And Controlled Atmospheres. Proc. 3nd Int. Working Conf. Stored – Prod. Entomol., Manhattan. Oct. 1983(1984)

[5] H. J. Banks. Stored Grain Research Laboratory, Division of Entomology, CSIRO, Canberra. Reprinted form: Champ. B. R., and Highley, E., Eds(1984). Proceedings of the Australian Development Assistance Course on the Preservation of Stored Cereals, Vol. 2. (CSIRO Division of Entomology: Canberra.)

[6] B. E. Ripp: leak detection in sealed Grain Storages: 1983 B. E. Ripp(ed) international symposiun Controlled Atmosphere and fumigation in Grain Storages

[7] D. X. bar editor jiwuzhan translating Frumentaceous CA Storage

[8] B. E. liper chief editor qianyulu translating Grain Storage CA and Fumgation Zhengzhou Institute of Technology 1986. 10

[9] Storage Bureau, Commerce Ministry 1987. 5, Australia Grain Storage Techology