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# Application Research on Sealing Technologies of CO<sub>2</sub> MA Granary and MA Grain Storage Technologies

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**Abstract:** The tendency of “green, ecology, harmony”, which is consistent with development of grain storage technologies in the world, was the goal of Chinese grain storage industries development. Such no-chemical grain storage technologies as Modified Atmosphere (MA), low temperature were accord with development of grain storage technologies. Based on lots of investigation and argumentation on CO<sub>2</sub> MA grain storage, Chinese government attached great importance on grain storage with no chemicals, and successfully constructed the first CO<sub>2</sub> MA grain storage demonstration depot in Mianyang on December 2007. During its construction, the conventional type of “Through-wall Joint-frame” had been rectified to the type of “double-frame”, which there were no scaffold holes in warehouse wall. Special gastight insulated doors and windows, axial fan windows and gastight insulated ventilation tube had been embedded and installed. Excellent gastight materials had been chosen to seal such places as warehouse walls, peak, the connection between ground with walls, craft holes, pipelines and so on, which influenced gastight performance of granary. Upon completion, inspection on MA granary settlement was done and it met with demands of construction qualities. Gastight performance was determined MA empty and field granaries by PT experimental method, and showed that all gastight performance met the demands of CO<sub>2</sub> MA granary, which the maximum half-life of empty granary was 490, and the minimum was 326, the maximum half-life of field granary was 497, and the minimum was 308. We could make a conclusion that the insulation performance of MA granary was better than ordinary granary by inspection on insulation performance of granary.

During MA granaries application, polyurethane and acrylic had been chosen as gastight materials with excellent performance by comparison carefully in Mianyang grain depot under state grain reserves, furthermore, the test method on gastight had been improved. Since 2002, Mianyang grain depot had made experiment on CO<sub>2</sub> MA grain storage for more than 2 years. Comparing with conventional grain storage, some researches had been carried out seriously, which focused on MA fumigation for pests control, grain qualities maintenance and so on. It had shown by experiment on CO<sub>2</sub> MA grain storage that fumigation with CO<sub>2</sub>, at the concentration of 70%–35% for 15 days, had the same effect with the conventional fumigation with phosphine, which could control and prevent pests growth completely. As being far away from pesticide resistance, it kept accordance with demands of grain storage with no-chemicals. Because CO<sub>2</sub> MA grain storage could postpone quality keeping period, alternation cycle and decrease the time for grain alteration, it would save lots of alteration fees and produce significant economic returns. Meanwhile, by preventing storemen far away from chemicals for grain storage, CO<sub>2</sub> MA grain storage protect physical and mental health of storemen. Moreover, it also protected environment from chemicals contamination, and had excellent social benefits.

**key words:** carbon dioxide, MA granary, grain storage

## 1 Sealing Technologies of CO<sub>2</sub> CA Granary

### 1.1 Special Treatments on Some Key Positions

1.1.1 Epoxy polyamide dope was used as sealing materials, and sprayed and coated with different concentration by different ways. It adhered onto granary wall without air bubble homogenously. After drying to film, there was no crack and holes.

1.1.2 Sealing treatment on the connection of granary walls and tip, ground and walls

**Table 1. Test results on gastight of MA empty granary and field granary**

No	pressure half-life of empty granary (seconds)	pressure half-life of empty granary (seconds)
12	336	333
13	340	338
14	338	316
15	340	351

was carried out mainly by polyurethane coatings, Polyester Fiber cosmos or Bolivian filament cloth. Before sealing and coating, wider

gap was filled with polyester foam or caulking compound. To meet the sealing requirement, equipping and coating should be taken again and again for sealing, and donet onto cracks, air bubble and holes.

1.1.3 Airtight attemperator doors and windows, axial fan and airtight attemperator ventilation were made especially by professional factories. And during equipment, its frame was sealed tightly with the connection of walls by covering underground.

1.1.4 Enhancing airtight seam gum and sealant. There was gap of 1 cm wide and 18 cm deep among each vaulted board in MA granary. As reinforced concrete distortion is normal, it happened to alter. All kinds of operation holes also influenced on airtightness of granary. So, sealing treatment was done. To prevent granary from gas leak, which was caused by house distortion, cement mortar meeting relative expansion requirement was filled into crack in every vaulted boards, and then PH-T elastic epoxy resin seam gum was poured from top leakage for excellent sealing effect. Open steam sealant was used for sealing at entrance and exit, axial fan hole, manhole, supplying CO<sub>2</sub> hole and electric pipeline for grain inspection.

**Table 2. Test results on heat insulation of MA and ordinary granary**

Type of granary	MA granary(°C)	Control granary(°C)	Remarks
Temperature at 1 meter above granary surface	36.0	36.0	
Outter temperature at top of granary	45.0	45.0	Thermometer reached the top of granary
Temperature at superior string of vaulted board	30.5	41.0	Thermometer reached the superior string
Temperature in vaulted peak	30.5	34.0	
Temperature at inferior string of vaulted board	30.5	34.0	Thermometer reached the inferior string
Temperature at brim wall towards the sun	36.0	36.0	Thermometer reached the brim wall
Temperature at brim wall against the sun	32.5	32.5	Thermometer reached the brim wall
Environmental temperature	32.5	32.5	
Temperature in granary	29.8	31.8	Data on inspection grain condition

Type of granary	MA granary(°C)	Control granary(°C)	Remarks
Below 2.1 meters	0.41	0.42	
K value Beyond 2.1 meters	0.47	0.48	W/m <sup>2</sup> . K
The peak of house	0.22	0.51	

## 2 Sealing Technologies Research on MA Granary

During CO<sub>2</sub> MA granary application for 5 years, as the phenomena of expansion and contraction, which happened due to natural sedimentation and temperature alteration, some cracks at the gap in granary vaulted boards and manhole were found, meanwhile, aging and deformation appeared in gum at doors and windows. These factors influenced on airtightness performance of MA granary, and its gastight could not reach the requirement. So our depots have carried out extensive and deep researches on how to choose excellent airtight materials and apply with advanced gastight technologies. After such series of treatment having been taken, as carrying necessary improvement on granary, gastight performance had been reached to requirement. And MA technologies had been made sure for effective application and active generalization.

### 2.1 Enhancing Gastight of Board Gap and Manhole

Such sealing materials as ordinary concrete, foreign concrete, epoxy resin, polyurethane and acrylate were used for filling up board cracks and manhole in our depot for the past few years. It has been found that whether ordinary concrete or foreign concrete, all of them had some characteristics on hardness in winter and tenacity in summer. There were some cracks after hardness in winter, and granary began to leak gas. After tenacity in summer, some concrete fell onto pavement or grain mass. So it could have some bad influence on sanitation in granary, even make some pollution in grain. In winter, epoxy resin became harder and brittle, and then some cracks appeared and granary gastightness was influence.

Polyurethane was gave better gastightness and extension quality than acrylate, however, the price of polyurethane was 2 – 3 times more than acrylate. If only application with polyurethane, the cost of grain storage would be raised. So combination of polyurethane with acrylate was applied in our depot. Meanwhile, for assuring the qualities of treatment, after consultation with

several companies, finally Chengdu Haizhinian Waterproof Science Reserve Co. Ltd., which embraced strong technologies and excellent service qualities, was chosen. Ten MA granary board cracks and manholes had been taken some treatment during 2004 – 2006. After gastightness test, gastightness of MA empty and filled granary all were beyond 4 minutes, and met the requirement gastightness.

## 2.2 Reconstructing Electric Pipeline in MA Granary

Electric pipeline in ten MA granaries was done in 2005, 2006. At the same time, package sealing has been carried on for electric pipeline, including changing equipment lamp on vaulted board gap to granary walls surrounding, adjusting incandescent bulb to fluorescent lamp, and filled lamp socket out, so gastight qualities in granary had been intensified.

## 2.3 Replacing Sealant of MA Granary Doors and Windows

In 2007, some sealants with good sealing qualities and excellent texture were chosen to replace others sealants aged and deformed in ten MA doors and windows. So the gastight of granary doors and windows had been intensified and met the requirement.

## 2.4 Reconstructing Windows in MA Granary

Stainless steel plates had been used in the doors and windows of CO<sub>2</sub> MA granary designed in the first period. Tightening and sealing gudgeon should be taken to complete by high-altitude operation. It was not only difficult to take in practice, but also having hidden danger in safes. So under the premises of not influence on gastight of doors and windows, windows have taken some reconstruction in MA granary during the first period. To reconstruction from plate type to connecting rod pushing, it made sure for operation in safe, and decreasing storemen works intension.

# 3 Test on Grain Storage with CO<sub>2</sub> MA

## 3.1 Experimental Granary

3.1.1 No. 10 ordinary granary: It was 48 meters long, 24 meters wide, and 6 meters high, containing 3 895 t of long-grain nonglutinous rice, harvested in 2001, filled in depots on February, 2002. Grade of paddy was the third grade, moisture content was 12.7%, impurity rate 0.5%, so the paddy was regarded as being suitable for storage. Gastight performance of empty granary was 45, of filled granary was 41.

3.1.2 No. 12 MA granary It was 48 meters long, 24 meters wide, and 6 meters high, containing 4173 t of long-grain nonglutinous rice, harvested in 2001, filled on March, 2002. Grade of paddy was the third grade, moisture content was 12.3%, impurity rate 0.6%, so the paddy was regarded as being suitable for storage. Gastight performance of empty granary was 336, of filled granary was 333.

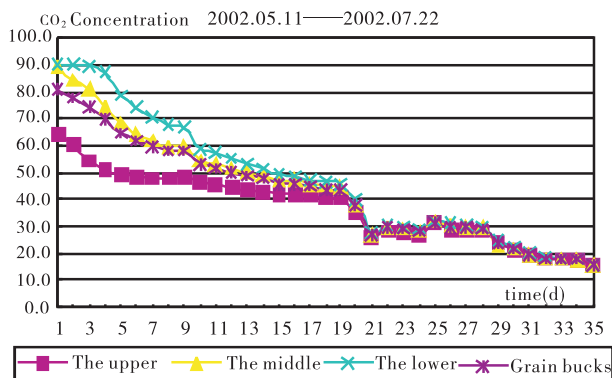
## 3.2 Effect on Pests Control by Fumigation

No. 12 MA granary was treatment granary, meanwhile ordinary granary was regarded as control group. Ten group test pests sample, including pesticide sensitive strain maize beetle, grain borer and red flour beetle, pesticide resistance strain rice weevil, grain borer and red flour beetle, its resistance index was 196 times, 204 times and 8 times, respectively than sensitive. Six group test pests had been equipped in No. 10 ordinary granary, which pest varieties was the same with No. 12.

No. 12 MA granary was filled with 10 t CO<sub>2</sub> of on May 11<sup>th</sup>, 2002. Its concentration decreased as Figure 1. Fumigation with AIP was done for pests in No. 10 ordinary granary. (by the way of intermission mixture fumigation at twice, AIP quantities of 21 kg, CO<sub>2</sub> quantities of 21 kg, sealed for 28 days). All test pests samples were taken outside from two granaries after 30 days. Lethal ratios of test adult pests was determined, and sent them to The pests control center of Chengdu grain storage research institute for inspection their lethal ratios again, meanwhile, lethal ratios of their eggs, pupae and larva have been inspected after culturing for 42 days by experimental methods. It has been shown from experimental inspection that all adult grain storage pests and insects at every period (egg, pupae and larvae) have been controlled in No. 12 and 10 granaries. The results indicated that the way, with 70% – 35% CO<sub>2</sub> concentration for 15 days in large storage house, could prevent and control these grain storage pests completely. It had the same pests control effects with fumigation with phosphine.

## 3.3 Influence CO<sub>2</sub> MA Grain Storage on Grain Qualities

Long-grain nonglutinous rice was loaded into No. 12 MA granary and No. 10 ordinary granary on March, 2002 and February, 2002 respectively. After filling the granary up, samples have been taken from different locations for inspection grain qualities. During grain storage,



**Fig. 1 CO<sub>2</sub> decrease tendency of concentration in MA granary**

their qualities was determined periodically, and some comparison analyses were carried out. The results of inspection are given in Table 1 and Table 2.

From data in Table 1 and Table 2, we could see that grain qualities in No. 12 were the same with in No.10 at the time of entrance granary. And as grain storage time increased, there was low difference in such physical indexes as moisture content, impurity and so on, but large difference in such chemical indexes as fatty acid value, viscosity and germination ratios. After paddy stored in No. 10 ordinary granary for 10 months, its fatty acid value raised from 19.1mgKOH/100g to 23.9 mgKOH/100g, viscosity value decreased from 14.8 mm<sup>2</sup>/s to 10.6 mm<sup>2</sup>/s, germination ratio decreased from 77% to 34%, taste panel scores decreased from 81 to 78. Meanwhile, in No. 12 MA granary, paddy's fatty acid value raised from 19.7mgKOH/100g to 21.8 mgKOH/100g, viscosity value decreased from 14.6 mm<sup>2</sup>/s to 10.9mm<sup>2</sup>/s, germination ratio decreased from 80% to 52%, taste panel scores decreased from 81 to 78. After paddy stored in No. 10 ordinary granary for 20 months, its fatty acid value raised from 19.1 mgKOH/100g to 26.1 mgKOH/100g, viscosity value decreased from 14.8 mm<sup>2</sup>/s to 8.7 mm<sup>2</sup>/s, germination ratio decreased from 77% to 3%, taste panel scores decreased from 81 to 73. Meanwhile, in No. 12 MA granary, paddy's fatty acid value raised from 19.7 mgKOH/100g to 22.4 mgKOH/100g, viscosity value decreased from 14.6 mm<sup>2</sup>/s to 8.6 mm<sup>2</sup>/s, germination ratio decreased from 80% to 36%, taste panel scores decreased from 81 to 75. After paddy stored in No. 10 ordinary granary for 28 months, its fatty acid value raised from 19.1 mgKOH/100g to 32.0 mgKOH/100g, its qualities was not fit for storage continuingly, and needed be alternated

to grain market. Meanwhile, in No. 12 MA granary, paddy's fatty acid value raised from 19.7 mgKOH/100g to 27.3 mgKOH/100g, it still could be able to be in storage.

From data above, it has been shown that such paddy qualities alteration velocity in MA granary was slower than in conventional storage, as fatty acid value raising, viscosity decreasing, germination decreasing and taste panel scores decreasing. At the same conditions, paddy's storage time for proper qualities could be postpone appropriately. So MA could postpone paddy storage period relatively, decrease the time of alternating into market. It would save lots of alternation fee for our country, and had great economic returns.

#### 4 Application with MA Grain Storage in Our Depot

Since experiments on CO<sub>2</sub> MA grain storage began in 2002, check&accept successfully in 2004, so far all ten MA granaries constructed in our depot applied CO<sub>2</sub> MA technologies for grain storage. During these technologies application for more than 5 years, by lots of summarizing and explorations, we has comprehended deeply that CO<sub>2</sub> MA technologies for grain storage had better advantages than conventional grain storage technologies.

4.1 During conventional grain storage, when AIP has been applied for pests control, there will be phosphine residue in grain and environments contamination. However, with CO<sub>2</sub> MA for grain storage, it could protect mankind health from chemical residue in grain and environments contamination effectively.

4.2 As single application with AIP to control pests for many years in conventional grain storage, and chemicals application in no standard sometimes, pesticide resistance of pests has being increasing, and it became more and more difficult to control and prevent insects pests. However, CO<sub>2</sub> had stronger ability to control such grain storage pests with high pesticide resistance as lice and rusty grain beetle as well. It provided with new pests control technologies and practice ways for inhibition pesticide resistance in large house grain storage

4.3 As a kind of grain storage technologies with no contamination and nuisanceless, MA CO<sub>2</sub> grain storage technologies kept accordance with requirement for green foods from the publics and tendency of grain markets.

4.4 As innovation further of grain distribution system and alteration of relation between

supply with need in grain market, grain qualities kept in no stabilization, such as large impurities, high moisture content and pests contamination. Because of excellent gastight of MA granary, pests would be very difficult to enter granary. Meanwhile, at certain CO<sub>2</sub> concentration in MA granary, hiding performance of pests made them be MA granary away. So MA grain storage technologies provided promise for grain reserved in safe at state grain storage depots, where could arrived at the index of four-free during whole year.

4.5 As CO<sub>2</sub> application with MA grain storage, there would be lots of time for MA granary in sealing stage every year. If computer for inspecting grain storage condition kept normal, storemen would not need to enter granary for inspecting grain condition frequently. So the work qualities and intensification has been lowered relatively. Meanwhile, far away from chemicals for grain storage, it was helpful for storemen health.

4.6 Successful application with CO<sub>2</sub> MA for grain storage had such advantages for enhancing international competitive strength, as raising competitive strength in market for grain alternation, increasing economic returns, intensifying suitability of Chinese grain export to international market.

## 5 Prospects

MA with CO<sub>2</sub> has no social effects of pollution for grain storage, which could control pests effectively, inhibit mould growth and postpone grain aging. Moreover, it has avoided effects of chemicals harmful to storemen, contamination to grain and environment. As fumigation with PH<sub>3</sub>, it would take eroding on equipments in granary (especially inspection system on grain condition). Contrary with fumigation with PH<sub>3</sub>, it could prevent devices from eroding to save the fee for treatment materials eroded by PH<sub>3</sub>, meanwhile, it also could avoid from others factors such as pesticide resistance raising of grain storage pests. Since being in consistent with the tendency of demands for green foods from the publics and development of grain markets, there was large and potential social values and economic returns. Being fit for the demands of grain storage development tendency of “high quality, high benefit, rich nutrition, low spoilage, low contamination, low cost”, these ways would be extended and spread further as scientific development and economical advancement.

**Table 1. Inspection results on paddy's qualities in No.10 granary (ordinary granary)**

Data	Brown rice rate (%)	Head-Ricerate (%)	Moisture content (%)	Impurity (%)	Fatty acid value (KO-Hmg/100g)	Viscosity (mm <sup>2</sup> /s)	Taste panel scores (mark)	Germination rate (%)	Whether fit for storage or not	Color and luster
2002.5	76.8	53.6	12.3	0.7	19.1	14.8	81	77	yes	normal
2002.10	76.9	55.2	12.4	0.5	22.3	13.2	79	58	yes	normal
2003.3	76.1	53.0	12.6	0.6	23.9	10.6	78	34	yes	normal
2003.9	75.8	52.6	12.8	0.7	27.0	8.8	73	17	yes	normal
2004.3	76.0	51.5	12.9	0.6	26.1	8.7	73	3	yes	normal
2004.9	75.8	50.0	13.0	0.6	32.0		71	0	yes	normal

**Table 2. Inspection results on paddy's qualities in No.12 granary (MA granary)**

Data	Brown rice rate (%)	Head-Rice rate (%)	Moisture content (%)	Impurity (%)	Fatty acid value (KO-Hmg/100g)	Viscosity (mm <sup>2</sup> /s)	Taste panel scores (mark)	Germination rate (%)	Whether fit for storage or not	Color and luster
2002.4	76.9	54.0	12.7	0.7	19.7	14.6	81	80	yes	normal
2002.10	76.7	54.3	12.3	0.7	20.9	12.3	79	63	yes	normal
2003.3	77.0	53.5	12.7	0.8	21.8	10.9	78	52	yes	normal
2003.9	77.0	53.0	12.8	0.6	24.5	8.8	77	41	yes	normal
2004.3	76.5	52.8	12.9	0.6	22.4	8.6	75	36	yes	normal
2004.9	76.2	50.0	12.9	0.7	27.8	8.6	75	24	yes	normal
2005.3	76.9	52.0	12.8	1.0	26.4	/	75	/	yes	normal
2005.9	76.8	51.4	12.5	0.8	27.3	/	75	/	yes	normal

**Table 3. Inspection results on paddy's qualities in No 10 granary (ordinary granary)**

Data	Brown rice rate (%)	Head-Ricerate (%)	Moisture content (%)	Impurity (%)	Fatty acid value (KOHmg/100g)	Viscosity (mm <sup>2</sup> /s)	Taste panel scores (mark)	Germination rate (%)	Whether fit for storage or not	Color and luster
2002.05	76.8	53.6	12.3	0.7	19.1	14.8	81	77	yes	normal
2002.10	76.9	55.2	12.4	0.5	22.3	13.2	79	58	yes	normal
2003.03	76.1	53.0	12.6	0.6	23.9	10.6	78	34	yes	normal
2003.09	75.8	52.6	12.8	0.7	27.0	8.8	73	17	yes	normal
2004.03	76.0	51.5	12.9	0.6	26.1	8.7	73	3	yes	normal
2004.09	75.8	50.0	13.0	0.6	32.0	/	71	0	yes	normal

**Table 4. Inspection results on paddy's qualities in No 12 granary (MA granary)**

Data	Brown rice rate (%)	Head-Ricerate (%)	Moisture content (%)	Impurity (%)	Fatty acid value (KO-Hmg/100g)	Viscosity (mm <sup>2</sup> /s)	Taste panel scores (mark)	Germination rate (%)	Whether fit for storage or not	Color and luster
2002.04	76.9	54.0	12.7	0.7	19.7	14.6	81	80	yes	normal
2002.10	76.7	54.3	12.3	0.7	20.9	12.3	79	63	yes	normal
2003.03	77.0	53.5	12.7	0.8	21.8	10.9	78	52	yes	normal
2003.09	77.0	53.0	12.8	0.6	24.5	8.8	77	41	yes	normal
2004.03	76.5	52.8	12.9	0.6	22.4	8.6	75	36	yes	normal
2004.09	76.2	50.0	12.9	0.7	27.8	8.6	75	24	yes	normal
2005.03	76.9	52.0	12.8	1.0	26.4	/	75	/	yes	normal
2005.09	76.8	51.4	12.5	0.8	27.3	/	75	/	yes	normal

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## References

- [1] Dai Linli. How to Grain Storage, 2003(4)
- [2] Tu Jie et al. Paddy's qualities by CO<sub>2</sub> Controlled atmosphere comparing with Conventional storage, Grain Storage, 2003(6)
- [3] Ma Honglin et al. Pretiminary discussion on CO<sub>2</sub> Controlled atmosphere technologies, proceedings of state grain reserve science and technologies in west – East region, 2003(5)
- [4] Ma zhongping et al. Application of CO<sub>2</sub> controlled atmosphere technologies in our depot, Grain Storage, 2006(3)