0904

Research Progress on Modified Atmosphere Technologies in China

Fu Pengcheng and Tao Cheng

Abstract: We summarize here the progress on Modified Atmosphere (MA) technologies that have been made since the 1960's in China, including natural low-oxygen and artificial low-oxygen, application with deoxidizers, "double-low" and "three-low" storage, MA with carbon dioxide and nitrogen-enrichening, and sealing materials and technologies for grain storage. Research Progress on MA Technologies in China has vaulted into the ranks of the advanced countries in the world.

Key words: China, grain, modified atmosphere

Compared with conventional techniques of grain storage to prevent and control insect pests, inhibit growth of grain fungi, and postpone changes in grain quality, MA, which works through altering gas elements in well sealed granaries, is a more important and complicated technology for grain storage. In the last several years, many continuing studies have been conducted by the regional grain administration throughout China, and many application technologies have been developed and significant progress has been made. Research Institutes and Academies have solved the key technologies for MA application by brainstorming projects.

1 Research on Natural Low-Oxygen and Artificial Low-Oxygen

Oxygen concentration can be lowered and carbon dioxide concentration can be increased through natural respiration of grain and microbes. (1) natural low-oxygen. In 1974, experiments on natural low-oxygen for pests control in grain storage were made at a grain depot under the grain administration of Jia county, Zhejiang province. The study showed that rice weevil, flour beetles, and sawtoothed grain beetle were controlled in 48 hours because the concentration of oxygen was lower than 0.5%. When the moisture and temperature of the grain was higher, the rate at which oxygen concentration was lowered increased. Different grains and grain products had different rates at which oxygen was lowered. For example, wheat > japonica rice > Keng paddy > flour[1]。 (2) artificial low-oxygen. ① In 1972, an experiment on low-oxygen for grain storage was conducted by the Second grain depot under Nanchang Grain Corp., Jiangxi province. It showed that the concentration of oxygen had been lowered to 3% – 6% by the end of the experiment, that circulation of low-oxygen with carbon burning could be done easily and at low cost, and this resulted in good pest control [2]. ② In 1974, an experiment on deoxidation by microorganisms was conducted at the grain depot under the grain administration of Jia county, Zhejiang province. It showed that by cultivating *Saccharomyoes carlsberqcnsis* on bran and chaff, one kilogram of substrate could consume 30 – 50 liter of oxygen every 24 hours[3]。 ③ In 1975, an experiment on speeding deoxidation by microorganisms was conducted by the grain administration of Xiangtan region, Hunan province. It showed that the content of carbon dioxide is 5 – 6 times higher than control group when cultivating *Mucor* mucedo on rice bran to lower oxygen concentration, and the effect would be better by cultivating Saccharifying Strains and Yeast on rice bran substrate to lower oxygen concentration[4].

2 Application Technologies Research on Free-Oxygen Absorber for Grain Storage

Application technologies research on Free-Oxygen Absorber for grain storage began in the 1980s in China. ① In 1982, relevant research was conducted by the Second purchasing and supplying grain depot and Fudan University biology department, Shanghai City. It showed that packaging rice with a Free-Oxygen Absorber packet would better inhibit fungi and improve storage quality than vacuum storage, but the Free-Oxygen Absorber is expensive[5]. ② In 1983, Lu Xiyu et al., showed that an iron deoxidizer had more potential than sodium hyposulfite[6]. ③ In 1985, Huang Zhiliang et al.

Chengdu Grain Storage Research Institute, State Administration of Grain Reserves 601131

showed that polyethylene polyester film had better sealing performance than polyethylene film for rice. The moisture and temperature of grain had little effect on deoxidant effects, and heat and moisture produced during the deoxidization process had little impact on grain storage stability[7]. ④ In 1986, Ni Zhaozhen et al. conducted studies on the composition of different iron deoxidizers, the absorbing abilities of deoxidizers with different carriers, actual oxygen consumption, and the amount of time it took to absorb the oxygen. ⑤ In 1987, He Qihua et al. conducted experiments on salted peanut and in-shell peanut storage with deoxidizers, and they showed that germination ability and other physiochemical indices were always better than with conventional techniques of grain storage [9]. ⑥ In 1988, they showed that F_X – B deoxidizer had excellent application prospects.

3 Research on "Double-low" and "Three-low" Storage

As with the development of fumigation with hydrogen phosphide and grain storage technologies with low temperature and MA in the 1980s, "double-low" and "three-low" storage has been developed in China and been improved and perfected constantly. Here "double-low" storage means grain storage technologies combining "low-oxygen and low-fumigants", and "three-low" storage means combination grain storage technologies, including "low-temperature", "low-oxygen" and "low-fumigants". In recent years, development of these technologies has advanced further, and as an example of application on grain storage, has been written into the China Grain Professional Criterion "Technical Criterion of Grain and Oils Storage".

① In 1976, Wang Zhengqun et al. conducted experiments showed that the combination of natural low-oxygen with low-fumigants provided effective grain storage [11]. ② In 1980, experiments with the combination of natural low – oxygen and low concentration PH_3 fumigation determined the quantities of PH_3 required[12]. ③ In 1980, Liu Weichun wrote a paper "application technologies on 'three-low' grain storage", which introduced requirements and application methods for "three-low" technology[13]. ④ In 1980, through the paper "MA synergism on pH_3 fumigation and its technologies application", Liang Quan et al. showed that lowering the oxygen concentration to 12% and increasing the carbon dioxide concentration to 4% – 8% improved PH_3 efficacy significantly for control of the five main grain storage beetles. The synergism index would account for pests group resistance against PH_3, but the relativity between synergism index with pests group had not been found. When postponing the sealed time the effect of pests control will be increase. Combination MA with pH_3 fumigation can degrade fumigants quantity and improve the effect of pests control, Thus they can be taken as a kind of fumigation strategies against resistance pests [14]. ⑤ In 1980, in the paper "research about carbon dioxide influence on pests control with low concentration PH_3", Qiu Shijie et al. indicated that when the concentration of carbon dioxide and oxygen were respectively higher or lower than their homologous concentration, the lethal ratio of red flour beetle and maize beetle with PH_3 was improved. At a temperature of 30℃, carbon dioxide content greater than 11.8%, and oxygen concentration below 10.6%, fumigation with PH_3 at 0.009mg/L for 3 days caused adult pest death. However, in a normal atmosphere, the same effect would be achieved at 0.015mg/L, so AlP quantity can be saved 40%[15]。 ⑥ In 1980, according to the research on "MA and grain storage pests control", Liang Quan et al. showed that at a grain temperature of 20℃ and moisture content below 15%, common adult beetles could be completely controlled. At an oxygen concentration of 5%, the time would be more than 27 days. At 3%, the time would be more than 21 days. At 2%, the time would be more than 16 days. The time to death would be halved if grain temperature was raised 5℃. ⑦ In 1980, according to "discussion on different oxygen concentration and effect of insecticide under MA" conducted by Zhe Jiang grain research institute, they found that when concentration of oxygen was below 2%, the exposure time of maize weevil, red flour beetle, sawtoothed grain beetle, and lesser grain borer would be about 96 hours. In the range of the limited lethal oxygen concentration of 2% – 5%, the lethal ratio was in direct proportion with the exposure time, and time was inversely related with moisture. If carbon dioxide was filled up with 2% – 5% content of oxygen, the lethal time of tested grain pests would be shortened, and have obvious synergism. But when the concentration of oxygen below 2%, then filled carbon dioxide up would not have obvious synergism. Relative pest sensitivity against low-oxygen was sawtoothed grain beetle > flour beetle > maize weevil > lesser grain borer and adults > larvae > egg > pupae[17]。 ⑧ In 1980, according to the paper of "discussion on low-oxygen low-fumigants and grain sealing storage" made by grain administration of Fengxian county, Shanghai city, they showed that when oxygen concentration decreased to 3% and carbon dioxide raised to 7% – 8%, each 25 – 35 ten thousands kilograms grain need one kilogram AlP [18]. ⑨ In 1985, according to "summary of comprehensive application technologies on 'three-low' grain storage" made by Jiangxi grain and oils grain storage Corp., four – way operations were tested, such as deoxidization by sealing→pest control by fumigation → temperature decrease by aeration→keeping low temperature; temperature decrease by aeration→pest control by fumigation→temperature decrease by aeration →keeping low temperature; pests control by fumigation (or chemicals mixture) → temperature decrease by aeration→keeping low temperature; putting low temperature grain into granary →pest control by fumigation (or chemicals mixture) → temperature decrease by aeration→keeping low temperature[19]. ⑩ In 1985, Jin Yinggui reported that the criterion requirement on "double-low" grain storage technologies would be established in Chengdu city.

4 Research on MA Technologies with Carbon Dioxide

Since the 1960s, many systematic studies on MA technologies with carbon dioxide have been conducted in China, including effect of pest control with CO_2, CO_2 synergism effect on fumigation with PH_3, CO_2 inhibition effect on grain storage mould, effect on grain qualities alteration with CO_2, and qualities alteration after MA with CO_2. In the last 10 years, much further research has been conducted.

① In 1997, Li Qiantai et al. conducted research on effects of different CO_2 concentrations (15%, 20%, 25%, 30%, 35%, 40%, 45%) on grain storage pest control at different temperatures (32℃, 28℃) and relative humidity (70%, 50%), and showed that there was an obvious effect at a CO_2 concentration of 15%[21–23]. ② In 2002, Deng Yongxue et al. exposed lesser grain borer adults and eggs, larva, pupae, and adults of confused flour beetle to 35% CO_2 and 11% O_2, 35% CO_2 and 21% O_2, 75% CO_2 and 11% O_2, 75% CO_2 and 21% O_2 for 12, 24, 36, 48, 60, 72, 84, 96, 108, and 120 hours, respectively, and showed that adult lesser grain borers were sensitive to these MA conditions and LT_{50} values were 34.6, 42.0, 18.6, and 17.8 hours respectively. Adult confused flour beetles were tolerant to 35% CO_2, 11% O_2 and 35% CO_2, 21% O_2 MA conditions, after treatment for 120 hours, and the lethal ratio was below 12%. All of the eggs and larva were sensitive to these four kinds of MA conditions. Pupae had stronger tolerance to 35% CO_2、11% O_2 than 35% CO_2、21% O_2, and their LT_{50} was 2248.3 hours and 124.5 hours respectively. The order of confused flour beetle sensitivity to MA conditions was as follows: egg > larve > pupae > adult[24]. ③ Based on a number of previous studies, four CO_2 MA grain storage demonstration granaries were built in Mianyang, Sichuan Province, and designed by Chengdu grain storage research institute. Excellent pests control with CO_2, inhibition of mould and postponing grain qualities alteration have been achieved in actual granaries. ④ Chengdu grain storage research institute also has undertaken design and construction of another four large CO_2 MA depots in Shanghai, Jiangxi, Jiangsu, and Anhui province, of which the largest single capacity reached up to seven thousands tons and the total capacity under CO_2 MA reached up to 21 500 tons.

5 Research on MA with Nitrogen – enrichening

Following application of MA with CO_2, many studies on MA with nitrogen-enrichening have been carried out. ① During 1968 ~ 1970, the practice of sealing grain with a polyethylene sheet for storage had been adopted by the grain storage Corp. in Shanghai. About ninety millions tons of grain has been preserved by enrichening with nitrogen after vacuum, there were no heating, no pests, and no mould in the grain bulks during storage [26]. ② In 1972, in an experiment on rice storage with nitrogen – enrichening conducted by the grain and oils storage Corp. in Shanghai, it was shown that the quality of rice increased as the concentration of nitrogen increased, and *Penicillium* and *Aspergillus candidus* growth increased in final period of storage when concentration of nitrogen below 95%[27]. ③ In 1975, through an experiment on low-oxygen storage conducted by the Chengdu grain storage research institute, it showed that there was not only low cost by nitrogen-enrichening, but also such qualities as reducing sugar, non-reducing sugar, viscosity, pH of rice water, and content of dry matter in rice water were better than in the control group[28]. ④ In 1976, an experiment on deoxidization and nitrogen-enrichening with molecular sieves for grain storage was reported by the grain and oils Corp. in Xiangtan region, Hunan province. ⑤ In 1982, in the paper "the experiment on deoxidization and nitrogen-richening with 5Åmolecular sieve for grain storage" by Shanghai grain storage Corp., they showed that the sieve generator, which produced quantities at $20m^3/h$ and concentration beyond 98%, could be used for grain storage to control pests[30]. ⑥ In 1983, through the paper "research on deoxidization and nitrogen-richening with molecular sieve for grain storage", Jiang Zhongzhu showed that grain qualities could be maintained better and the content of oxygen could be degraded faster this way[31]. ⑦ In 1983, through the paper "research on carbon molecular sieve nitrogen generator", Cheng Zhiyuan showed that a carbon molecular sieve generator worked better than, and it had such advantages as low energy consumption, simple operation technology, and low cost. When concentration of nitrogen was 98%, the producing nitrogen ratio and recovery rate were better[32]. ⑧ An experiment on inhibiting mould growth was conducted by the grain administration of Fushun county, Sichuan province, and showed that pests could be controlled effectively when decreasing the concentration of oxygen to the limitation of 2% by the RSL – 180 nitrogen generator[33]. ⑨ In 2005, at the Nanjing depot directly under the centre grain storage Corp., studies showed that grain storage pests could be inhibited effectively and grain temperature in the upper bulks could be decreased by producing nitrogen with a nitrogen generator so that concentration of nitrogen circulation fumigation reached 95% under the sheet for 16 – 20 days,[34]. ⑩ Since 2008, the China grain reserve Corp. extended the capabilities of MA with nitrogen to 0.5 million tons at ten depots directly under the centre grain storage Corp. in Lower-and-Middle Section of Yangtze River and south China, with plans for an additional 1.5 million tons by 2010.

6 Research on Sealing Materials and Technologies for Grain Storage

It was the key for the MA operation to be successful and low cost to determine whether maintaining the airtight quality of the grain warehouse was beneficial or not. Through numerous experiments, relevant points with airtight quality have been solved in China by researches on MA technologies with airtight materials and economic analysis.

①In 1979, in the paper "grain storage with carbon dioxide MA", Tang Zhengjia et al. measured carbon dioxide leakage through a plastic sheet [35]. ② In 1980, through research on sealing materials and technologies conducted by Shanghai grain research institute, the performances of plastic sheet and complex sheet, made in China, were tested, and the results from full – scale experiments were reported. ③ In 1983, conglutinate technologies of sheets in sealed storage were discussed by JiuLongPo district grain Corp., Chongqing city[37]. ④ In 1983, preliminary research on airtight material in granary was conducted by Zhang Ziquan[38]. ⑤ In 1983, Xu Yuanzhang et al. showed that two layers of No 10 asphalt and paper chart ash had better airtight performance by determining the air tightness of four coating materials[39]. ⑥ In 1984, Teng Jianping et al. determined gas permeation ratio through different films, oxygen consumption by paddy with different moistures, the requirement time of paddy anoxybioticly under well sealed conditions, paddy with different moisture contents sealed by polyvinyl chloride film of different widths, and oxygen content in grain bulks in storage [40]. ⑦ In 1984, in the paper "ways adhering plastic film with granary walls" by the storage department in grain administration of Mianyang region, Sichuan province, experiments on adhesives and paints were undertaken. Experiments were conducted on plastic plate gluing ways, gluing ways with adhesives, gluing ways with paints and sealing ways by olefin with comprehensive considerations of air tightness, strength of gluing, and cost. Original investment of plastic plate gluing ways was high, however, if used for enough times, costs could be spread over time[41]. ⑧ In 2002, in the construction of Mianyang MA grain storage granary, Sichuan province, the difficulties of selection of sealing materials and technologies operation were overcome by Tu Jie et al. They found that the half – loss time at 500Pa in airtight performance of an MA empty granary reached beyond 12 minutes, and in a kernel granary it reached 5 minutes and 16 seconds.

7 Summary

As China's national economy develops rapidly, green foods have become popular by more and more people. MA has been regarded as a non-chemical storage technology which has been accepted generally in the world and will have more and more application in China.

Reference

[1] Depot directly under JiaShan county Grain Administration in ZheJiang province, Preliminary experiment on grain storage in the condition of "oxygen lack naturally", SiChuan grain&oil science and technologies, 1974(2):20 – 26

[2] The Second grain depot of NanChang grain corporation in JiangXi province, Experiment on grain storage by oxygenation in air, SiChuan grain&oil science and technologies, 1972(4): 18 – 23

[3] Science and research team of depot directly under JiaShan county Grain Administration in ZheJiang province, Experiment on application microbes to lower oxygen concentration for grain storage, SiChuan grain&oil science and technologies, 1976(1):34 – 37

[4] Science and research room of XiangTan Grain Administration in HuNan province, Application microbes to accelerate oxygenation. SiChuan grain&oil science and technologies, 1975(3): 48

[5] The Second grain stock&supply station in ShangHai city, Teaching and researching team of microbes department of FuDan university, Preliminary discussion on application chemicals. Grain Storage, 1982(6):21 – 26

[6] Lu Xiyu, Zhu Datong, Wang Jianong, et al. Research on application deoxygenor for grain storage. Proceedings of the third grain&oil storage in China, 1983:220 – 227

[7] Huang Zhiliang, Lin Lixin, Shi Boheng, et al. Application deoxygenor for storage rice and food. Grain Storage, 1985(2):26 – 34

[8] Ni Zhaozhen, Wu Jinxin. Preliminary research on oxygen consumption by deoxygenor, Grain Storage, 1986(6):21 – 25

[9] He Qihua, Lin Zhigang, et al, Preliminary experiment on salted peanut and fresh peanut by deoxygenor, The newsletter of grain&oil storage science and technologies, 1987(5):36 – 44

[10] Lu Xiyu, Yan Yongshen, Huang Depeng, Paper on grain storage by self-mastery deoxygenor, Journal of the Chinese cereals and oils association, 1988(4):28 – 36

[11] Wan Zhenqun, Grain sealing storage at low oxygen and low chemical concentration, SiChuan grain&oil science and technologies, 1976(4): 34 – 35

[12] JinTang County TaiPing grain supply center in SiChuan province, Experimental paper on pest control combination oxygen lackness naturally with low concentration of AlP, Proceedings of the second national grain storage professional conference, 1980:130

[13] Liu Weichun, application technologies of grain storage by "three-low", Grain Storage, 1980(2):13 – 19

[14] Liangquan et al. Discussion on CA synergism to PH_3 fumigation and its technical procedure, Grain Storage, 1980(1):1 – 11, 17

[15] Qiu Shijie, Zhang Zhenqiu, Huang Xueming et al, Influence of Carbon Dioxide to low concentration of PH_3, Proceedings of the second national grain storage professional conference, 1980: 76 – 89

[16] Liang Quan, Hua Dejian et al, CA and grain storage pests control, Proceedings of the second national grain storage professional conference, 1980:127

[17] Grain storage lab of ZheJiang province grain research institute, Discussion on the effect of pests control at different oxygen concentration in different condition, Proceedings of the second national grain storage professional conference, 1980:128

[18] Fengxian County Grain Administration in ShangHai city, Discussion on grain sealing storage at low oxygen and low concentration, Proceedings of the second national grain storage professional conference, 1980:129

[19] Jiangxi province grain&oil storage co., Summary of application "three-low" technologies for grain storage, Newsletter of grian&oil storage science and technology, 1985(3):1 – 6

[20] Jin Yingui, "doubt-low" grain storage technologies rules draft in ChengDu, Newsletter of grian&oil storage science and technology, 1986(3):56

[21] Li Qiantai, Song Yongcheng, Research on grain storage pests control with carbon dioxide CA (1). Grain Storage, 1997(5):3 – 10

[22] Li Qiantai, Song Yongcheng, Research on grain storage pests control with carbon dioxide CA (Ⅱ). Grain Storage, 1997(6):7 – 12

[23] Li Qiantai, Song Yongcheng, Research on grain storage pests control with carbon dioxide CA (Ⅲ). Grain Storage, 1998(2):8 – 13

[24] Deng Yongxue, Zhao Zhimo, et al. Research on borers and beetles control at high concentration of CO_2 CA, Grain Storage, 2002(1):3 – 6

[25] Tu Jie, Ma Honglin, et al, Construction of CO_2 CA grain storage project in MianYang depot, State Grain Reserve, Grain Storage, 2002(4): 43 – 47

[26] Shanghai city grain storage co., Experiment of rice storage with filling nitrogen into vacuum, SiChuan grain&oil science and technologies, 1972, 2

[27] Shanghai city grain storage co., Experiment of rice preservation by "filling nitrogen into vacuum", SiChuan grain&oil science and technologies, 1972(1):29 – 33

[28] Chengdu grain storage research institute, State grain reserve administration, et al, Experiment on rice storage in lackness oxygen condition, Proceedings (1) of science paper, 199

[28] Science and research room of XiangTan Grain Administration in HuNan province, Experiment on grain storage by molecule sieve collection Nitrogen, SiChuan grain&oil science and technologies, 1976(4):32 – 33

[30] Grain storage research room of ShangHai city grain storage co., the first grain supply centre in

ShangHai city, Experiment on application 5A molecule sieve collection Nitrogen, Grain Storage, 1982(5):20 – 24

[31] Jiang Zhongzhu, Liu Xiqi, Qi Derong, Research on molecule sieve collecting Nitrogen, Grain Storage, 1983(5):15 – 20

[32] Chen Zhiyuan, Nitrogen production with carbon molecule sieve, Grain Storage, 1983(5):21 – 23

[33] FuShun county Grain Administration in SiChuan province, Paddy storage by filling Nitrogen, Proceedings of the second national grain storage professional conference, 260

[34] Xu Decun, Application pests control by nitrogen in large and wide warehouse, Proceedings of the sixth national grain storage professional conference, 213

[35] Tang Zhengjia, Zhou Zhumei, Grain storage by carbon dioxide, Grain Storage, 1979(4):1 – 14

[36] Shanghai city grain science and research institute, Storage by oxygen lackness——research on sealing technologies and materials, Proceedings of the second national grain storage professional conference, 1980:155 – 167

[37] Grain Co. in ChongQing city JiuLongPo region, Jiangbei county Grain Administration in ChongQing city, Film gluing technologies in the procession of sealing storage, Proceedings of the third national grain storage professional conference, 1983:361 – 364

[38] Zhang Ziquan, Preliminary research on sealing coating material of granary, Proceedings of the third national grain storage professional conference, 1983:373 – 375

[39] Xu Yuanzhang, Li Wenhui, Air tightness determination of four kinds of coating materials of granary walls, Grain Storage, 1983(4):33 – 34

[40] Teng Jianping, Application PVC film in sealing storage, Grain Storage, 1984(4):26 – 30

[41] Storage Department of Mianyang region Grain Administration in SiChuan province, Mianyang Grain Administration in SiChuan province, Mianyang city Fenggu grain supply center in SiChuan province, Methods of combiantion PVC film with granary walls, Grain Storage, 1984(1):41 – 43