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AlP Low Dosage Recirculation Fumigation under Film through PH_3 Dynamic Deliquescence

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Abstract: Three fumigation methods were investigated in this paper. The results showed that the recirculation fumigation under film through PH_3 dynamic deliquescence effectively reduced fumigation spaces, saved CO_2, decreased the moisture content losses of grain bulk, killed stored – grain insects effectively, and the phosphide residue in grain was lower than the national health standard. For the recirculation fumigation under film through PH_3 dynamic deliquescence, the storage cost was 53 % cheaper than that of whole warehouse PH_3 dynamic deliquescence, and 89 % cheaper than that of whole warehouse recirculation fumigation. In addition, the recirculation fumigation under film through PH_3 dynamic deliquescence realized the grain storage objective that is safer, economical, practical and in favor of environment protection.

Key words: low dosage, dynamic deliquescence, recirculation fumigation under film

Since 1998, all of newly built and extension depots have been equipped with new four grain storage technology which include grain inspection, mechanical aeration, recirculation fumigation, and grain cooling. Particularly, the recirculation fumigation greatly decreased the labor intensity during fumigation work, reduced the contacting time with toxic gas, improving grain storage scientific management level in depots. However, because of poor air-tightness of warehouses, inconvenient manipulation of gas-producing type recommended by new grain storage technology and higher application cost, the use of the warehouse and grain storage benefit was negatively affected. In order to resolve the poor air-tightness of the warehouses, the weak killing effect on pest insects, the overuse of fumigant dosage, the higher application cost, and so on, the joint key technologies R&D group between Zhoukou Grain Depot, State Grain Reserves and Zhengzhou Institute of Technology was established in March, 2003, and the program "AlP Low Dosage Recirculation Fumigation under Film through PH_3 Dynamic Deliquescence" was put forward, which harmoniously combined sealed grain storage technology and recirculation fumigation technology. The "AlP Low Dosage Recirculation Fumigation under Film through PH_3 Dynamic Deliquescence" can exert the advantages of recirculation fumigation technology which can realize the quick and even gas distribution in warehouses, keep excellent air-tightness of the grain mass sealed below plastic film, significantly reduce fumigation spaces and application dosage, and enhance the fumigation effect. By combining dynamic deliquescence, the technology is brought to perfection, and its manipulation is quick, convenient, economical, effective, safe and in favor of environment protection.

1 Experimental Materials and Methods

1.1 Experimental Materials

1.1.1 Experimental warehouses

The experimental warehouses included No. 27, 29 and 16 warehouses located in Zhoukou Grain Depot, State Grain Reserves. The former two warehouses were newly-built horizontal warehouses in 2000, whose specification was 60m × 30m. Warehouse air-tightness, namely pressure half-life time, was 43 seconds under 500Pa. There were 8 groups of in-floor U-channel main air – ducts each with 3 branches installed in the warehouse, 4 air intakes set at each side of the warehouse which could realize aeration at two sides. The air-ducts layout plan

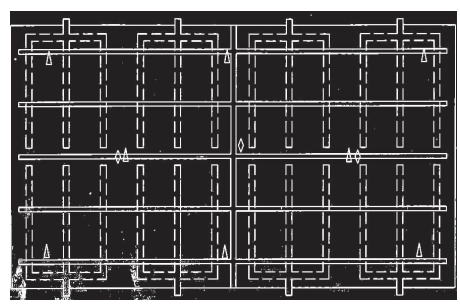

Fig. 1 The air-ducts, air return tubes, and air-testing sites disposal ichnography in warehouse.

Zhoukou Grain Depot, State Grain Reserves, Zhoukou Henan 466002, *China*

is shown in Fig. 1. No. 16 warehouse was a newly – built horizontal warehouses in 1998, whose specification was 58m × 24m. There were 3 groups of main air-ducts under floor each with 4 branches installed in the warehouse. The structure of the experimental warehouses was broken – line roof truss, and the filling high was 6m.

1.1.2 Experimental grain

The experimental grain was bulk mixed wheat. The grain surface was sealed by plastic film, and the other were expressed in table 1.

Table 1. The basic grain condition in No. 27, 29 and 16 warehouses

No.	Grain storage beginning time Year. month	Quantityt	Storage style	Bulk densityg/L	Moisture content %	Impurity %	Visciditycst	Gluten hygroscpic content %
27	02.2	8856	sealed	790	12.5	0.6	10.4	214
29	02.1	8916	bulk	786	12.5	0.5	7.7	209
16	01.7	6130	bulk	780	12.0	0.7	5.9	213

Note: The broken – lines indicate air-ducts, the solid lines indicate air return tubes; indicate air-testing sites in No. 27 warehouse; indicate air-testing sites in No. 29 warehouse.

1.1.3 Experimental instruments and materials

Recirculation system: the mobile recirculation fumigation system made in Shenzhen dashi stock Co., Ltd., whose power is ≤1kW, aeration ability 500 – 1 000m^3/h, full pressure 800 – 1 000Pa.

Outdoor PH_3 generator: XZL – IV type, made in Shandong Jinxiang grain machinery factory.

PH_3 gas detector – alarm: HL – 210 type, made in Beijing jialianglao technology and trade Co., Ltd.

Radiofrequency electronic welding machine: KW – 2500T type, made in Tianjin Beixin electronic equipment Co., Ltd.

Air pressure meter: YEP – 101 type, made in Handan xinyu instrument and meter Co., Ltd.

Plastic film: PVC press – extension film whose thickness was 0.2mm, made in Tianjin No. 4 plastic products factory.

Air return tubes: PVC tube, φ50mm, φ30mm, made in Shangshui county plastic tube factory.

Fumigant: 56% AlP tablet, baolianglin brand, made in Shandong Jining chemical and industrial experiment factory.

CO_2 gas: purity was 98%, 25kg/bottle, made in Pingdingshan fertilizer factory.

1.1.4 Experimental insects

The experimental insects were *Rizorpertha dominita*, *Tribolium confusum*, *Cryptolestes turcicus*, *Sitophilus zeamais*.

R. dominita and *S. zeamais* were collected in Zhengzhou. Both of them have been cultured with wheat for several years in stored – grain insects control laboratory in Zhengzhou Institute of Technology. *T. confusum* and *C. turcicus* were collected in Xinjinag and Zhengzhou respectively. Both of them have been cultured with whole wheat flour adding 5% yeast for several years in stored – grain insects control laboratory in Zhengzhou Institute of Technology.

1.2 Experimental Methods

1.2.1 Air return tubes disposal under plastic film

Because the grain would be stored by single surface seal with plastic film, the grain surface was sealed with plastic film after the grain condition was stable. The air return tubes was buried under the grain surface 300mm in advance. The air return tubes constituted 1 main tubes and 5 branch tubes arranged as "丰" type. The main tube diameter was 50mm, no holes on its surface. The main tube was arranged in the center of the warehouse, and its two ends were coupled with recirculation main duct on the warehouse wall. The diameter of 5 branch tubes was 30mm. The branch tubes were parallel arranged two sides of the main tubes, spacing 5m between 2 neighboring branch tubes. There were little holes on the branch tubes surface whose diameter was 2mm. There were 6 circularity holes every interval 1m in the branch tubes within 15m from the main tube, and 6 circularity holes every interval 0.5m in the branch tubes outside 15m from the main tube. The air return tubes layout pattern under plastic film is shown in Figure 1, and the gas recirculation fumigation process under film is shown in Figure 2.

1.2.2 The locations of gas concentration sampling sites and sampling times

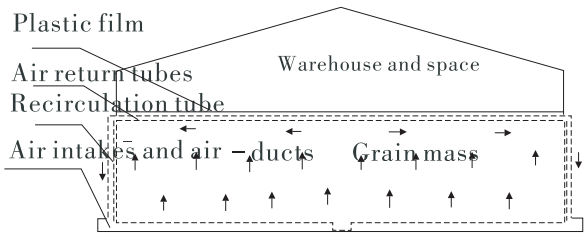

Fig. 2 Airflow circulation sketch map for recir culation fumigation process under film

8 sampling and detecting holes were placed on the grain surface film in No. 27 warehouse. Each hole had upper, middle and bottom layer depths which were located at 1.0m, 3.0m and 5.5m under the grain surface. The gas concentration detecting was conducted on the grain surface film in warehouse. A gas detecting site was respectively set in eastern and western side grain mass, locating at upper, middle and bottom layers in No. 29 warehouse. 5 gas detecting sites were placed in No. 16 warehouse. The PH_3 concentration at each detecting site and fumigation space in No. 29 and No. 16 warehouses was monitored on schedule by leading the gas through plastic pipes to an outdoor gas sampling instrument. The gas detecting sites layout patterns in each warehouse is shown in Figure 1.

The gas concentration was detected 20h after AlP application in each warehouse, two times each day for at the first 15 days, then once per day. If the PH_3 concentration was above 100mL/m^3, gas concentration detecting could be continued. One to two times gas concentration monitoring should be done before finishing film sealing, to check the PH_3 concentration maintaining background state in the warehouses.

Table 2. Fumigation concentration detecting values in No. 27 warehouse unit: mL/m^3

Day	1	2	3	4	5	6	7	8	Mean
1	131	248	323	168	274	322	204	205	234
2	291	314	328	311	363	403	369	365	343
3	364	359	401	381	442	489	432	468	417
4	390	427	459	423	488	516	512	493	464
5	318	316	354	330	392	413	376	374	359
7	296	291	316	306	376	383	355	344	333
14	230	239	273	226	305	292	270	243	260
21	163	179	202	159	219	210	192	166	186
28	116	134	151	118	155	153	139	118	136
34	73	90	100	75	90	100	89	73	86
55	45	56	60	49	56	60	55	45	53

Table 3. Fumigation concentration detecting values in No. 29 warehouse unit: mL/m^3

Day	Western site	Eastern site	Space site	day	Western site	Eastern site	Space site
1	135	61	50	14	173	196	177
2	211	121	231	15	161	175	150
3	262	256	242	16	143	153	128
4	346	292	270	17	133	142	108
5	318	324	300	18	124	133	103
6	312	316	298	19	109	118	87
7	306	310	293	20	102	112	82
8	279	299	275	21	96	106	84
9	263	281	273	22	90	97	89
10	244	271	270	23	87	99	91
11	227	263	266	24	70	80	73
12	205	237	220	25	55	57	25
13	183	212	175				

Table 4. Fumigation concentration detecting values in No. 16 warehouse unit: mL/m^3

Day	1	2	3	4	5	Mean	Day	1	2	3	4	5
1	62	78	69	58	67	12	264	270	259	200	185	236
2	153	160	138	151	152	150	13	210	225	189	169	153
3	362	367	345	345	357	355	14	163	170	144	131	120
4	433	434	438	406	440	430	15	137	152	125	125	113
5	320	337	309	300	285	310	16	118	128	103	119	100
6	264	279	243	257	232	255	17	96	107	85	113	89
7	206	211	158	197	168	188	18	88	99	78	101	78
8	136	149	108	110	95	120	19	79	93	70	87	65
9	295	264	252	301	290	280	20	72	87	64	76	59
10	452	410	480	395	406	429	21	63	80	57	62	48
11	370	333	388	289	260	328						

1.2.3 Sealing the grain surface

In order to further enhance warehouse airtightness, eliminate the effect of outdoor adverse environment condition, Zhoukou Grain Depot adopted grain surface film sealing method to store the grain. The detailed manipulation was the following: A batten, 7cm × 4cm width, was fixed alongside the inside wall at 6m filling height in the warehouses, and a sealed slot pipe was inlayed in the middle of the batten. The sealed slot pipe was 4cm spacing from the wall whose interior edge had a 25mm × 15mm rectangular groove, 25mm spacing from the wall, with its opening faced upwards. For the sake of conveniently sealing grain mass, alleviating the labor intensity, such as covering and uncovering film manipulation, the plastic film was divided into 8 pieces according to warehouse plane. The pieces of film was joined each other by 10cm

width wooden skeletal frames on whose two sides were mounted groved pipe. 4m width press-extension film was jointed together by radiofrequency electronic welding machine. Then, the film was pressed into the grove pipe using glue bar piece by piece, pouring the melted wax to seal the slot pipes on the ambient wall. The groove pipes in wooden skeletal frames were sealed by adhesive tape. This was simply called as "wooden skeletal frame piece sealing method".

To ensure the quality of film sealing, the air-tightness under the surface sealing sheet was tested by negative pressure method. The tested result showed that the pressure half life time was 147 seconds under 500Pa in No. 27 warehouse, according with the requirement for fumigation and grain storage.

1.2.4 The insect cages pre-burying

The insect cages were made beforehand from φ50mm × 120mm plastic pipes whose two ends were sealed by 120 eyes sieve silk. The cage was filled to 1/2 capacity with wheat in advance. Twenty standardized cultured testing insects, *R. dominita*, *T. confusum*, *C. turcicus*, *S. zeamais*, 7 – 14 day adults, respectively were put into the insect cage which was then sealed with sieve silk for experiment. The cages, with locater and retrieval cords attached, were buried 50cm below the grain surface at each gas concentration detecting site. The insects death condition was inspected after gas dispersing, and the cages with *R. dominita* and *S. zeamais* were again taken to incubation box (28 ± 2℃, 70% ± 5% r. h.) in the laboratory. Adult insects emergence condition from the fumigation test cages was again inspected in the laboratory after 40 days.

1.2.5 Fumigation scheme

The grain surface was sealed with plastic film in No. 27 warehouse. Adopted fumigation scheme was fumigant application by outdoor air intakes, dynamic deliquescence and low dosage fumigation under film. Fumigant dosage was 1.1g/m^3 (calculating by practical grain mass). Each intake was filled with 1.5kg AlP tablet, with 12kg AlP tablet for 8 intakes altogether. Continuous recirculation was operated for 48h after fumigant dosage application, then the recirculation blower was run 3h each day for at least 15 days.

Routine storage and whole warehouse recirculation fumigation was used in No. 29 warehouse. Adopted fumigation scheme was dynamic deliquescence recirculation fumigation combining grain surface and air – duct fumigant application. Fumigant dosage was 2g/m^3 (calculating by the whole warehouse volume). 16kg of AlP tablets were applied on the grain surface. Each intake was filled with 2.5kg of AlP tablets, or 20kg of AlP tablets for 8 intakes altogether. 36kg of AlP tablet was applied in the whole warehouse. The recirculation fumigation blower was started as No. 27 warehouse right after fumigant dosage application.

Routine storage was also used in No. 16 warehouse. However, the adopted fumigation scheme was whole warehouse recirculation fumigation using outdoor PH_3 generator to produce PH_3 gas. Fumigant dosage was 1.44g/m^3 (including supplement fumigant dosage). 20kg of AlP tablet and 1 000kg of CO_2 was applied in the whole warehouse as the initial dosage, and 6kg of AlP tablet and 300kg of CO_2 was added as a supplemental dosage after 5 days. Continuous recirculation was operated for 20h after initial fumigant dosage application, then recirculation was run 3h each day for at least 15 days.

If the fumigant concentration could not be maintained above 100mL/m^3 for 15 days after the first fumigant application in each warehouse, supplement fumigant application must be added depending on actual gas concentration conditions of each warehouse.

1.2.6 Organic phosphorus residues detecting in grain after fumigation

In order to compare the relationship between the fumigant application dosage and the organic phosphorus residues in grain, the organic phosphorus residue content in fumigation grain was detected after routine fumigant application dosage and low dosage under film.

1.2.7 The effect of film sealing on stored grain temperature change

In order to explore the effect of film sealing on stored grain temperature change, No. 27 and 29 bulk warehouses, which had the same warehouse structure, grain storage time and grain condition, with similar grain temperatures, were compared. When the air temperature was increasing in spring, the grain surface was sealed with film in No. 27 warehouse, and the grain mass was still kept as unsealed bulk with open headspace in No. 29 warehouse. The stored grain temperature change in the two warehouses was inspected by the same computer at the same time.

2 Results

2.1 Fumigation Effect of Different Fumigation Methods

PH_3 concentration sample monitoring re-

sults in No. 27,29 and 16 warehouses were listed in Tables 2 – 4. According to the detecting results, PH_3 concentration change trend was drawn in Figures 3 – 5.

Table 2 and Figure 3 had clearly showed that only one time 12kg fumigant application could maintain PH_3 concentration above 100mL/m^3 for

Table 5. Temperature change comparison betweenfilm sealing and bulk grain mass

Testing day	No.	Warehouse temperature ℃	Average temperature at each site, ℃				Average grain temperature ℃	grain temperature difference
			Upper	Upper – middle	Middle – bottom	bottom		
5.12	27	23.5	17.7	15.1	15.1	14.6	15.6	0.8
	28	24.1	18.7	16.1	16.5	15.7	16.8	
5.19	27	26	18.3	15.1	15.3	14.8	15.9	1
	28	25.8	19.2	16.2	16.6	15.7	16.9	
5.26	27	26.9	19.8	15.4	15.5	15	16.4	1.1
	28	27.4	21	16.5	16.5	15.9	17.5	
6.2	27	28.5	21.1	17	17.1	16.2	17.9	1
	28	29.2	22.5	18.3	18	16.9	18.9	
6.9	27	30	22.6	15.8	15.7	15.3	17.3	1.4
	28	30.8	24.1	16.9	17.1	16.8	18.7	
6.16	27	29.2	23.3	16.1	15.9	15.5	17.7	1.2
	28	31	24.6	17.1	17.3	16.7	18.9	
6.23	27	29.4	24.3	17.2	16.5	16.2	18.6	1.1
	28	30.7	25	18.4	18	17.3	19.7	
6.30	27	29.6	24.1	16.9	16.6	16	18.4	1.4
	28	30.3	25	18.5	18.2	17.3	19.8	
7.7	27	29.8	23.7	17.1	16.7	16.1	18.4	1.2
	28	30	24.8	18.3	17.9	17.2	19.2	
7.14	127	29.8	24.3	17.5	16.6	16.4	18.9	1
	28	30.9	25.7	18.6	18.1	17.4	19.9	
7.21	127	30.7	25.3	17.9	16.9	16.7	19.2	1.2
	28	31.5	27.3	18.8	18.3	17.1	20.4	
7.29	127	31.2	26	18.4	17.1	16.8	19.6	0.7
	28	31.8	27.1	18.9	18.4	16.9	20.3	

32 days because of the excellent air – tightness in No. 27 warehouse. PH_3 fumigation concentration reached the highest level on the fourth day, and the average fumigation concentration reached 464 mL/m^3. According to PH_3 fumigation concentration distribution on the second and third days, the rate between the highest and the lowest concentration were respectively 0.72, 0.73. Decreasing ratio per day was 2.7% – 3.5%, which showed that PH_3 concentration could reach even distribution in the warehouse after 2 to 3 days recirculation. The PH_3 concentration decreasing trend was stable at 8 detecting sites during sealing period.

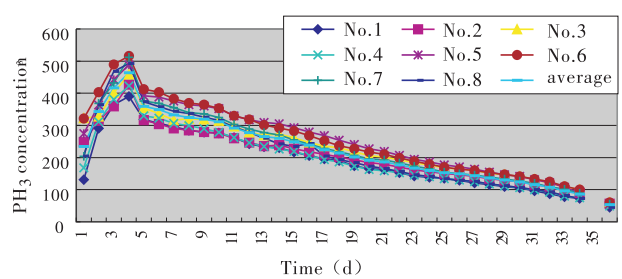

Fig. 3 PH_3 concentration change trend during fumigation sealing period in No. 27 warehouse

Table 3 and Figure 4 clearly showed that a one – time fumigant application can maintain PH_3 concentration above 100mL/m^3 for 18 days in No. 29 warehouse. The highest concentration

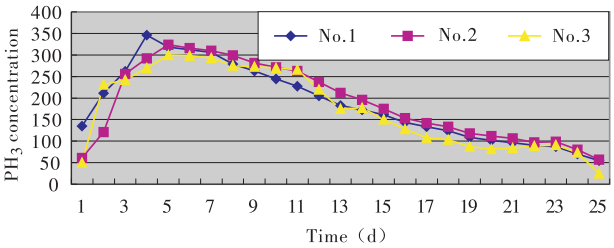

Fig. 4 PH_3 concentration change trend during fumigation sealing period in No. 29 warehouse

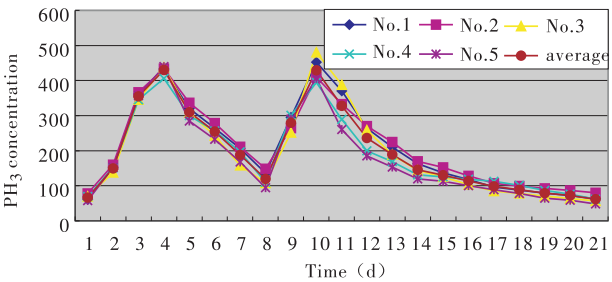

Fig. 5 PH_3 concentration change trend during fumigation sealing period in No. 16 warehouse

in eastern part, western part and space above grain surface in the warehouse were respectively 324, 346 and 300 mL/m^3. However, the PH_3 concentration in No. 29 warehouse decreased faster than that in No. 27 warehouse, and decreasing ratio per day was 8.5% – 10%.

After only 8 days after dosage, the PH_3 concentration decrease to 120mL/m^3 in No. 16 warehouse. In order to enhance the fumigation effect, an additional 6kg of AlP tablets and 300kg of CO_2 was added as supplemental dosage on the 8th day. Thus, 26kg of AlP tablets and 1 300kg of CO_2 was applied during two fumigant applications in Warehouse No. 16, then PH_3 concentration above100mL/m^3 was maintained for 16 days. Among the three warehouses, the PH_3 concentration in No. 16 warehouse decreased fastest. During the whole recirculation fumigation period, the highest average concentration respectively reached 429 and 430 mL/m^3 (see Table 4 and Figure 5).

2.2 Fumigation Effect Inspecting

The pre-buried insect cages in each warehouse were taken out of the grain mass after fumigation. Both the insects death condition and the adults emergence condition in the cages with *R. dominita* and *S. zeamais* and grain samples sampled at each detecting site after 40 days incubation in the laboratory were inspected, and no live insects were found. The results proved that all insects were killed in all warehouses, thus, the fumigation efficacy was excellent. However, one live insect was found at one side door in No. 29 warehouse and on two northern windowsills of No. 16 warehouse. Thus, although the whole air-tightness in the warehouses reached the lowest standard (40 seconds), there still existed local positions with poor air-tightness. The toxic gas leaked from these positions resulting in the PH_3 concentration decreasing, which allowed a few individual insects at some developmental stage of some species of insects survive the fumigation. The phenomenon did not occur in No. 27 warehouse which adopt recirculation fumigation under film. Further more, low dosage, relatively uniform concentration distribution and low fumigation cost were realized. Consequently, it could be speculated that the air-tightness standard in present warehouses only satisfied with the lowest requirement for killing insects. In order to enhance the fumigation effect and reduce fumigation cost, some effective measures should be further taken to improve the air-tightness standard. Additional inspections with workers using sensitive phosphine detectors immediately after fumigations begin to locate major points of significant leakage, then resealing those leaks immediately, may help fine tune the sealing of each warehouse to increase half-life times of 90 sto 120 seconds or higher, like the 147 seconds of the tightly sealed Warehouse No. 27.

Three key factors for high fumigation efficacy are excellent air-tightness, maintaining uniform fumigant concentrations above lethal dosage and retaining lethal concentrations for the desired exposure time. Thus, the air-tightness in warehouses is the primary requirement for maintaining fumigation concentration and its sealed duration. Only if the air-tightness in warehouses reaches higher level, can higher fumigation concentration and its sealed duration be maintained, and the ideal fumigation effect be realized. However, the present poor air-tightness in some warehouses can't completely satisfy that the fumigation will not kill the insects.

By sealing the grain surface with film in Zhoukou Grain Depot, State Grain Reserves, the air-tightness of the warehouses were strongly enhanced, allowing the harmonious combining of recirculation fumigation with grain surface sealing by film. This method could realize sealing grain surface, keep excellent air-tightness (even if serious leaks may exist in warehouse roofs, or walls above the 6 m grain storage levels), accelerate the gas quickly with even distribution in grain mass by recirculation, improve

the air-tightness in the grain storage part of the warehouses, reduce fumigation spaces and application dosage, and enhance the fumigation effect of recirculation fumigation under film. Using film sealing of 6m level grain surface can save much sealing expense of roofs and eaves of current warehouses, making air-tightness easier to maintain as warehouses weather and age during future decades.

2.3 Dynamic Deliquescence Producing Gas Method Resolved the Difficult Problems Such as Fumigant Residues Cleaning after the Whole Recirculation Fumigation, Inconveniently Buying CO_2 Gas, and Higher Fumigation Costs.

The recommended producing gas method in the three national standards and regulations relating to recirculation fumigation was PH_3 – CO_2 mixed gas filled in high pressure steel cylinders (steel cylinder formulation) and whole warehouse recirculation fumigation. However, the former application cost was very expensive, and the latter had the difficult problems such as fumigant residues cleaning after the whole recirculation fumigation, inconveniently buying CO_2 gas, higher fumigation cost, and the transportation inconvenience and costs, and handling safety of high pressure cylinders.

Three fumigation methods, the recirculation fumigation under film through PH_3 dynamic deliquescence, whole warehouse PH_3 dynamic deliquescence and whole warehouse recirculation fumigation, were investigated in Zhoukou Grain Depot, State Grain Reserves. The results showed that economic application cost and simple manipulation for the recirculation fumigation under film through PH_3 dynamic deliquescence was far better than that for whole warehouse PH_3 dynamic deliquescence and whole warehouse recirculation fumigation. The recirculation fumigation under film through PH_3 dynamic deliquescence properly resolvea the difficult problems such as higher cost of gas producing method recommended by national standards and regulations and tedious manipulation. Further more, considering safety and environment protection, the method saved man power, reduced cost, lessened environment pollution, enhanced fumigation effect, The fumigation under film method has great development and extension potential for warehouse storage across China.

Although the dynamic deliquescence gas producing method by applying fumigant in air ducts and grain surface was not recommended by related regulations, its economic application cost and simple manipulation made it be quickly extended. Particularly, since the dynamic deliquescence gas producing method did not need to add CO_2 gas. Then, the dynamic deliquescence gas producing method resolved inconvenience to buy CO_2 gas for backland and grass roots depots, incomplete reaction in PH_3 generator, inconvenient fumigant residues cleaning, long time fumigant application, and so on, meanwhile, reduced greenhouse effect generated from CO_2 gas in the world.

2.4 Advantages of the Recirculation Fumigation under Film through PH_3 Dynamic Deliquescence

2.4.1 Sealing the grain surface could improve the air-tightness in the warehouses

In view of the excellent fumigation effect, sealing the grain mass not only improved the air-tightness in the warehouses, reduced toxic gas leaking, lessened environment pollution, but also avoided the grain again being reinfested by insects, alleviated the negative effect of bad environment factors on stored grain, significantly reduced grain quality spoilage rate, cut down grain moisture content loss, debased fumigant contamination in grain, and enhanced grain storage benefit.

2.4.2 The recirculation fumigation under film could save fumigant, reduce fumigation cost.

The fumigation space was reduced to 3/5 of the warehouse volume and the air-tightness in the warehouses was improved after sealing grain surface. Then the low dosage fumigation could be carried out, and the fumigation dosage was greatly reduced to 1/3 of previous dosages. Because all the insects were killed during the fumigation, one fumigation may maintain no insects occurring for at least two years, and the storage cost was significantly saved.

2.4.3 Low dosage recirculation fumigation under film could reduce phosphide residues in grain

With a defined AlP dosage, the fumigation effect of long time sealing was better than that of short time sealing depending on PH_3 characteristics. Due to poor the air-tightness in the warehouses, to get an excellent fumigation effect, the AlP dosage must be increased which correspondingly increased grain storage cost and made the organic phosphorus residues in grain exceed standards. The grain detecting results in table 6 showed that high dosage fumigation

could increase the organic phosphorus residues in grain, while low dosage fumigation obviously decreased the organic phosphorus residues in grain, far lower than permitted organic phosphorus residues standards in the national health standard GB2715 – 81. Consequently, to get required fumigation concentration by using low dosage, good air-tightness in the warehouses or grain mass must be maintained or enhanced. In practice, excellent fumigation effect should mainly be realized by enhancing the air-tightness in warehouses or grain mass, not by increasing dosage.

Table 6. Phosphide residue content in grain detecting results after fumigation

Permitted phosphide residues content (calculating as PH_3)	≤0.05mg/kg
Low dosage recirculation fumigation under film in No. 27 warehouse	0.03
Whole warehouse PH_3 dynamic deliquescence in No. 29 warehouse	0.12
Whole warehouse recirculation fumigation in No. 16 warehouse	0.10

2.4.4 Sealing the grain surface could reduce moisture content loss, and enhance the depots' economic benefit.

In recent years, tracking comparative moisture content analysis for grain in sealed and unsealed grain mass taken out of the warehouses were conducted in Zhoukou Grain Depot, State Grain Reserves. The results showed that the moisture content of wheat in sealed grain mass was 0.5% – 1.0% higher than that of the wheat in unsealed grain mass when being taken out of the warehouses which had been stored for 4 years. For the 8 856t wheat in No. 27 warehouse, if the wheat price was calculated as 1.20 yuan/kg, just the reduced moisture content loss could increase economic benefit 53 136 yuan.

2.4.5 The effect of film sealing on grain mass temperature

Grain is very susceptible to high temperatures. The higher the storage temperature, the worse the effect on grain quality. The average temperature of grain mass sealed with film in No. 27 warehouse was 1.1 C lower than that of bulk grain mass in No. 29 warehouse (see Table 5). Film sealing decreased gas convection in the grain mass and the negative effect of bad outdoor environmental factors. Surface sealing enhances grain mass heat preservation ability, thus, improves maintenance of stored grain quality.

2.5 The Economic Benefit Analysis about AlP Low Dosage Recirculation Fumigation under Film through PH_3 Dynamic Deliquescence

The detailed expenditures of sealing grain mass, recirculation fumigation under film and whole warehouse recirculation fumigation were listed in table 7.

The table 7 showed that the detailed expenditure items of the recirculation fumigation under film through PH_3 dynamic deliquescence, whole warehouse PH_3 dynamic deliquescence and whole warehouse recirculation fumigation mainly included film purchasing cost, yearly depreciation cost, man power cost for covering the grain with film (covering the whole warehouse took 3 days by ourselves). The saved cost included artificially cleaning, fumigation cost (additional fumigation was not needed because there were no insects after one – time fumigation). Its social benefit was far better than whole warehouse recirculation fumigation. Benefits were reducing toxic gas leaking and organic phosphorus residues content in grain, maintained grain quality with higher selling price. Just the cost savings by reducing grain moisture content loss could make up the fumigation and film sealing cost. By calculating, for the recirculation fumigation under film through PH_3 dynamic deliquescence, the storage cost was 53 % cheaper than that of whole warehouse PH_3 dynamic deliquescence, and 89 % cheaper than that of whole warehouse recirculation fumigation.

Table 7. Fumigation cost comparison of different fumigation styles in three warehouses

No.	Gas method or position	Grain amount (t)	Dosage (kg)	Fumigant cost – (yuan)	CO_2 cost (yuan)	Film yearly cost (yuan)	Subsidy cost (yuan)	Total Cost (yuan)	Cost (yuan/t)
27	Recirculation fumigation under film – PH_3 dynamic deliquescence	8856	12	288	0	375	100	569	0.064

No.	Gas method or position	Grain amount (t)	Dosage (kg)	Fumigant cost – (yuan)	CO_2 cost (yuan)	Film yearly cost (yuan)	Subsidy cost (yuan)	Total Cost (yuan)	Cost (yuan/t)
29	Whole warehouse PH_3 dynamic deliquescence	8916	34	816	0	0	400	1216	0.136
16	Whole warehouse recirculation fumigation	6130	26	624	2730	0	200	3554	0..580

Note: The CO_2 price was 2.1 yuan/kg, AlP 24 yuan/kg. The recirculation fans operated for 60h; the small electricity cost was ignored. Sealing grain surface film, 300kg, actually cost 3000 yuan, but only 375 yuan per year when calculating as average for 8 years grain storage before unloading the grain. Air return tubes for fumigation under film actually had initial cost of 300 yuan; that cost can be spread over several years use, so the cost is so small, it could be ignored. For one fumigation every two years by the recirculation fumigation under film through PH_3 dynamic deliquescence, the average yearly cost per ton grain was $388 \div 2 + 375 = 569$ yuan.

3 Conclusions

AlP dynamic deliquescence, film sealing the grain surface, recirculation under film, low dosage fumigation, and other grain storage technologies, were harmoniously combined in Zhoukou Grain Depot, State Grain Reserves, commendably resolved present, practical and difficult problems, such as high recirculation fumigation cost, tedious manipulation, poor air-tightness, abd worker health and safety.

3.1 AlP dynamic deliquescence producing gas method did not require use of CO_2 gas, and the grain managers did not enter the warehouse to apply the fumigant, or cleanout fumigant residues. The method not only resolved high cost of buying CO_2 gas, inconvenient fumigant residues cleaning and other difficult problems, but also alleviated workers' labor intensity and higher fumigation cost, shortened the workers contacting time with toxic gas, simplified fumigant application manipulation procedure, and enhanced work efficiency.

3.2 Adopting single grain surface sealing and wooden skeletal frame piece sealing method

The method effectively resolved the difficult problem, i. e. extended grain surface not easy to be sealed in large-scale warehouse, and further greatly improved the air-tightness in the grain mass, reduced fumigation space and dosage, saved fumigation cost.

3.3 The technology, recirculation fumigation under film through PH_3 dynamic deliquescence, made organic phosphorus residues content low, reduced PH_3 gas leaking, fumigant contamination on grain and environment, and commendably maintained grain quality.

3.4 Storage characteristics of the sealed grain mass was stable after fumigation. It was not necessary to uncover the film and turn the grain, or operate mechanical aeration. The recirculation fumigation under film through PH_3 dynamic deliquescence avoided the grain being reinfested by insects. The complete efficacy (100% insects killed) from one fumigationresulted in no insects infestation in the warehouse for at least two years. Meanwhile, a mass of grain moisture loss during long-term open bulk grain storage, which resulted in significant grain market weight loss, was effectively resolved. The grain storage aim, that is safe, economical, practical and in favor of environment protection, was realized.

3.5 Because the technology used low dosage and reduced number of fumigations, saved CO_2 gas, integrative application economic and social benefit was greatly enhanced in depot.

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