任永林教授主持“安全高效熏蒸 助力节粮减损”特约国际专栏文章之五

DOI: 10.16210/j.cnki.1007-7561.2024.03.005
AGARWAL M, NEWMAN J, LI Y Y, 等. 富氮气调——磷化氢的可供替换技术（中英文）[J]. 粮油食品科技, 2024, 32(3): 55-68.
AGARWAL M, NEWMAN J, LI Y Y, et al. Nitrogen as an alternative to phosphine (Chinese and English versions)[J]. Science and Technology of Cereals, Oils and Foods, 2024, 32(3): 55-68.

富氮气调——磷化氢的可供替换技术（中英文）

Manjree AGARWAL[1], James NEWMAN[2], Yan-yu LI[3,4], Li GU[3], Bei-bei LI[3], Yong-lin REN[3]✉

（1. 西澳大利亚政府化学中心，澳大利亚，珀斯 WA 6102；
2. CBH 澳大利亚谷物有限公司，澳大利亚，珀斯 WA 6000；
3. 默多克大学 环境和生命科学学院，澳大利亚，珀斯 WA 6150；
4. 国家粮食和物资储备局科学研究院 粮食储运研究所，北京 100037）

摘 要：在粮食储藏上利用氮气的方法已经有 30 多年的历史，但直到最近经济有效的变压吸附（PSA）和膜分离（MS）制氮设备的出现，才使得该技术在储粮上使用成为可能。本研究首先在 25、30 和 35 ℃、99%、98%和 97%氮气的环境下，对小麦、大麦、燕麦、羽扇豆和油菜籽中的花斑皮蠹、赤拟谷盗、谷蠹和米象成虫和非成虫虫态进行了为期 4、3 和 2 周的实验室生物测定。然后在终端用户 Lake Grace 和 CBH（Cooperative BulkHandling）谷物进出口公司 Albany 出口港码头开展实仓验证，测定小麦、大麦和油菜籽中不同储粮害虫虫种和油菜籽瓢虫和肖叶甲类两种田间害虫的防治效果。同时对处理后的粮食品质进行了测定。实验结果表明，害虫死亡率随着氧气浓度降低、暴露时间和温度的增加而增加，富氮低氧在低温条件下不能 100%致死花斑皮蠹幼虫。氮气处理对磷化氢抗性和敏感品系储粮害虫防治效果没有差异。与其他粮种相比，在油菜籽中的防治效果更好。各种粮种的水分含量、蛋白质、含油量、淀粉和籽粒颜色品质指标均未受到影响。成功开发了富氮低氧商业规模应用模式，为磷化氢高抗性害虫治理提供了解决方案，满足市场日益增长对无害虫和无化学残留粮食的需求。

关键词：气调储藏；害虫治理；磷化氢抗药性；粮食品质；应用模式

中图分类号：TS205 **文献标识码：**A **文章编号：**1007-7561(2024)03-0055-14

网络首发时间：2024-05-13 18:27:37

网络首发地址：https://link.cnki.net/urlid/11.3863.ts.20240511.1616.005

收稿日期：2024-02-28
基金项目：澳大利亚政府合作研究中心项目——磷化氢的可供替换技术（CRC50147）
Supported: the Australian Government’s Cooperative Research Centre Program——Alternatives to Phosphine (No. CRC50147)
作者简介：Manjree AGARWAL，女，博士，高级研究员，研究方向为熏蒸剂和害虫防控。E-mail: magarwal@chemcentre.wa.gov.au
通讯作者：Yong-lin Ren，男，博士，教授，研究方向为产后生物安全和食品安全。E-mail: y.ren@murdoch.edu.au
英译中：李燕羽（国家粮食和物资储备局科学研究院 粮食储运研究所）
本专栏背景及第一作者、通讯作者、译者介绍详见 PC8-15，本文英文原文详见 P62-68

Nitrogen as an Alternative to Phosphine (Chinese and English versions)

Manjree AGARWAL[1], James NEWMAN[2], Yan-yu LI[3,4], Li GU[3], Beibei LI[3], Yong-lin REN[3]✉

(1. ChemCentre, Government of Western Australia, Perth WA 6102, Australia; 2. CBH Group Australia, Perth WA 6000 Australia; 3. College of Environmental and Life Sciences, Murdoch University, Perth WA 6150, Australia; 4. Institute of Grain Storage and Logistics, Academy of National Food and Strategic Reserves Administration, Beijing 100037, China)

Abstract: The use of nitrogen gas in grain storage has a history of over 30 years. However, it wasn't until the recent emergence of economically efficient pressure swing adsorption (PSA) and membrane separation (MS) nitrogen production equipment that this technology became viable for grain storage. This study first conducted laboratory bioassays over 4, 3, and 2 weeks on wheat, barley, oats, lupin, and canola seeds, exposing them to environments of 25 ℃, 30 ℃, and 35 ℃ with nitrogen concentrations of 99%, 98%, and 97%. The study focused on assessing the adult and immature stages of *Trogoderma variabile*, *Tribolium castaneum*, *Rhyzopertha dominica*, and *Sitophilus oryzae*. Subsequently, in-field verification was carried out at the Lake Grace terminal and the Cooperative Bulk Handling (CBH) grain export terminal in Albany, evaluating the efficacy of controlling various storage grain pests and field pests in wheat, barley, and canola seeds, as well as assessing the quality of treated grains. The results showed that pest mortality increased with decreasing oxygen concentration, increasing exposure time, and temperature. However, under low-temperature conditions, nitrogen-rich low-oxygen treatment did not achieve 100% mortality of *Trogoderma variabile* larvae. There was no significant difference in the efficacy of controlling storage pests resistant or sensitive to phosphine. Canola seeds showed better control efficacy compared to other grains. Furthermore, the moisture content, protein, oil content, starch, and grain color quality indicators of various grains were unaffected. A commercially scalable nitrogen-rich low-oxygen application model was successfully developed, providing a solution for controlling pests resistant to phosphine and meeting the growing market demand for insect-free and chemical residue-free grains.

Key words: controlled atmosphere storage; pest management; phosphine resistance; grain quality; application model

澳大利亚粮食产业在很大程度上依赖国际公认的磷化氢熏蒸处理，以保持其收成免受虫害，这是市场准入的一个重要标准。基于一系列合理因素，磷化氢熏蒸剂是用于控制收获后粮食虫害的主要技术。然而，在过去的 15~20 年里，很多害虫对其产生了严重抗药性，威胁其有效控制性和可持续性，从而危及粮食市场准入。因此，开发经济有效、使用方便的替换技术，降低耐药性并控制耐药性的爆发，以及在磷化氢可能完全失效的最坏情况下有可行的技术和系统备用，迫在眉睫。目前许多研究对替代方法进行了利弊评估[1-3]。

长期以来，气调一直被认为是一种很有发展前景的储藏物消杀方法[4-6]。氮气、二氧化碳或它们的混合物以可控的方式充入密闭空间内，置换或稀释密闭空间里的氧气。高浓度二氧化碳（40%或更高）对昆虫有毒。氮气无毒，但可用于置换氧气，形成氧气含量低于 1%的大气，能够对储粮进行消杀。作为磷化氢抗性管理策略的一部分，建议将氮气气调作为潜在的非化学替代处理方式，特别是变压吸附（PSA）技术的最新发展，可以相对便宜地现场制备大量氮气，使基于氮气的气调成为一个可行的提议。相比与熏蒸剂，这项技术有几个优点：

氮气占空气的 78%，空气是丰富的氮气来源；

氮气无毒；

大大降低了职业健康安全和环境风险；

提供“有机”且真正无残留的谷物；

无已知抗性风险；

与建筑材料无化学反应；

粮食出售前无需通风散气；

无需进行农药登记注册。

该项目旨在澳大利亚国家范围内开展对基于氮气气调的经济有效且技术使用方便进行研究，以对储粮进行保护和消杀，从而生产无虫粮，控制磷化氢抗性害虫，延长磷化氢的使用寿命，增加管理实践措施，符合市场要求以及环境和工作场所的健康和安全标准。该项目目标是让合作的澳大利亚粮食公司，如 CBH、Vitarra 和 GrainCorp，采用基于氮气气调技术。技术经验证后推广给其他大型储存组织和种植者。

实仓验证采用的是变压吸附制氮装置，首先在 50 t 筒仓（农场规模）上进行，然后在 2 500 t 实仓仓库上进行。

1 材料与方法

1.1 富氮低氧防虫效果和对粮食质量影响的实验室评估

1.1.1 富氮低氧对害虫的防治效果

实验室生物测定在默多克大学收获后植物生物安全实验室进行。将恒定浓度的氮气和氧气通入气体吹扫流动系统（图 1）处理昆虫，并在处理期间系统内保持低二氧化碳浓度。在 1~4 周的处理期间，每天监测两次氮气、氧气和二氧化碳的浓度。

在 20~30 ℃的温度下，处理小麦、大麦、燕麦、羽扇豆和油菜籽中各个虫态的米象、赤拟谷盗、谷蠹和花斑皮蠹，以及油菜籽中瓢虫和 Bronzed field beetles（*Aderium brevicorne*）的成虫虫态，氮气浓度范围为 95%~99%，氧气作为平衡气体。在暴露期结束后取出布袋样品，对成虫进行计数并移除，剩余的样品在(25±1) ℃和 65%RH 下继续培养。随后每周对出现的成虫进行计数，共 5 周，每次计数后不管是活的还是死的成虫都从样品中移除。

（1）在小麦、大麦、燕麦、羽扇豆和油菜籽中，25、30 和 35 ℃、99%、98%和 97%氮气环境下，对花斑皮蠹、赤拟谷盗、谷蠹和米象成虫进行了为期 4、3 和 2 周的实验室生物测定。

图 1 将恒定浓度的氮气和氧气通入气体充入系统内处理昆虫，同时在处理期间系统内保持低二氧化碳浓度。15 个圆柱体都装有已知量（1.8~2 kg）的谷物（小麦、大麦、燕麦、羽扇豆和油菜籽），柱体内在 6 cm 和 23 cm 的深度布置有平纹细布制成的密封小袋，袋内装有 40~50 g 即>200 头混合虫龄的储粮害虫成虫。

Fig.1 A gas purging flow system was used to treat the insects with constant concentrations of nitrogen and oxygen and maintained low carbon dioxide concentrations during the period of treatment. All 15 cylinders were filled with a known amount (1.8~2 kg) of grain (wheat, barley, oats, lupin and canola). A sealed sachet made of muslin cloth with 40~50 g of mixed age culture of stored grain insects with >200 adults were inserted at a depth of 6 and 23 cm.

（2）在小麦、大麦、燕麦、羽扇豆和油菜籽中，25、30 和 35 ℃、99%、98%和 97%氮气环境下，对谷蠹、米象和赤拟谷盗的所有非成虫虫态进行了 4、3 和 2 周的实验室生物测定。

（3）在小麦、大麦、燕麦、羽扇豆和油菜籽中，25、30 和 35 ℃、98%~99%氮气环境下，对花斑皮蠹的所有非成虫虫态进行了 4、3 和 2 周的实验室生物测定。

1.1.2 富氮低氧对粮食品质的影响

使用 FOSS Infratec 1241 谷物分析仪对小麦、大麦、燕麦、羽扇豆和油菜籽在 25、30 和 35 ℃、98%~99%氮气环境下处理前后进行品质分析。

1.2 Lake Grace 农场实仓实验

在西澳大利亚州 Lake Grace （–33.117, 118.607）附近 Doug Clarke 附属的农场仓开展实仓实验（图 2）。使用产量为 30 m^3/h 99.5%N_2 的变压吸附（PSA）制氮机，将氮气充入 75 t 储存小麦和油菜籽气密（$P^{1/2}$≥180 s）仓中，最终仓内氮气浓度为 97%~98%。首次实验是在温度为 20 ℃的小麦仓内进行的。评价了对储粮害虫的防治效果和粮食品质的影响，包括谷蠹、米象、赤拟谷盗成虫虫态和花斑皮蠹幼虫虫态。

随后在 35 ℃、97%氮气条件下的油菜籽仓中进行，评价了对 Bronzed field beetles、瓢虫和各个虫态的谷蠹、米象、赤拟谷盗和花斑皮蠹的防

治效果，使用滴定法测定了 2 个月的储存期内的颜色、含油量和游离脂肪酸值。

实验期间还评估了各种充气模式。

图 2　在西澳大利亚州 Lake Grace (33.117, 118.607)附近 Doug Clarke 附属的农场仓开展实仓实验。使用产量为 30 m^3/h 99.5%N_2 的变压吸附（PSA）制氮机，将氮气充入 75 t 储存小麦和油菜籽气密仓中。

Fig.2　The farm bin-scale nitrogen application trials were conducted at Doug Clarke's farm near Lake Grace (33.117, 118.607), Western Australia. A pressure swing adsorption (PSA) nitrogen generator (capacity of 30 m^3 of 99.5% N_2/hour) was used for purging nitrogen to wheat and canola bines (capacity of 75 tonne).

1.3　CBH Albany 谷物出口码头实验

在 CBH Albany 谷物出口码头（35°1′50.90″S 117°53′10.54″E）安装了一台 350 m^3/h 变压吸附（PSA）制氮机，制氮机与一排 10×10 000 t 的混凝土仓相连。本实验在 30~32 ℃下对 5×10 000 t 的混凝土仓进行充气，仓里装有新收获的油菜籽和大麦（图 3），感染了赤拟谷盗、瓢虫和 Bronzed field beetles。

用 98%氮气处理 2~3 周后，所有大麦和油菜籽进行了出口检查，对赤拟谷盗、米象和谷蠹所有虫态的防治效果和处理后大麦和油菜籽的质量进行了评价。

2　结果与分析

2.1　富氮低氧对害虫及不同磷化氢抗性的作用效果

（1）在小麦、大麦、燕麦、羽扇豆和油菜籽中，25、30 和 35 ℃、99%、98%和 97%氮气环境下，对花斑皮蠹、谷蠹、米象和赤拟谷盗的成虫和所有非成虫虫态进行了 4、3 和 2 周的实验室生物测定。害虫死亡率随着氧气浓度降低、暴露时间和温度的增加而增加。与小麦、大麦、燕麦和羽扇豆相比，富氮低氧在油菜籽中的防治效果更好（表 2）。

在 95%、97%和 99%的氮气和 25 ℃的条件下分别进行了 6、5 和 3 天处理可完全控制油菜籽中瓢虫和 Bronzed field beetles 的成虫虫态（表 1）。

（2）实验室生物测定表明，氮气处理对磷化氢抗性和敏感品系的谷蠹、米象和赤拟谷盗成虫和非成虫虫态的防治效果没有差异。

图 3　在 CBH Albany 谷物出口码头（35°1′50.90″S 117°53′10.54″E）安装了一台 350 m^3/h 变压吸附（PSA）制氮机，制氮机与一排 10×10 000 t 的混凝土仓相连。

Fig.3　A 350 m^3/hour PSA nitrogen generator has been installed at the CBH Albany grain export terminal (35°1'50.90"S 117°53'10.54"E). The generator is plumbed to a bank of 10×10,000 tonne concrete cells.

（3）在西澳大利亚州 Lake Grace （–33.117, 118.607）附近 Doug Clarke 附属的农场仓使用 PSA 制氮机实验中，利用 97%~98%氮气浓度在 20 ℃下，一周可完全致死谷蠹、米象和赤拟谷盗成虫，而控制它们所有虫态则需要 3 周。但发现还有 6%~10%的花斑皮蠹幼虫存活。

（4）随后 35 ℃下在油菜籽仓中实验表明，暴露于 97%氮气环境 7 天后，肖叶甲类（Bronzed field beetles）和瓢虫死亡率为 100%。对于谷蠹、米象、赤拟谷盗和花斑皮蠹所有虫态需要 2 周暴露时间。在 2 个月的贮藏期内，油菜籽的颜色、含油量和游离脂肪酸值没有变化。

表 1 不同温度下推荐氮浓度和暴露时间

Table 1 Recommended dosage of nitrogen and exposure period at different temperatures

储藏类型	粮种	虫种	*氮气浓度	*氮气浓度（有虫粮）	不同粮温下暴露时间	监测间隔期/d	所需的最低氮气浓度	装船等待期
筒仓	油菜籽	所有虫种成虫虫态	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	≥35 ℃，2 d ≥30 ℃，3 d ≥25 ℃，5 d ≥20 ℃，7 d	每天	顶部和底部为 98%	无
		收获期甲虫和象甲科			≥35 ℃，2 d ≥30 ℃，3 d ≥25 ℃，6 d			
		所有虫种全部虫态（不包括皮蠹类）			≥30 ℃，14 d ≥20 ℃，21 d			
		皮蠹类的全部虫态			≥35 ℃，14 d ≥30 ℃，18 d ≥25 ℃，25 d			
筒仓	小麦 大麦	所有虫种成虫虫态	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	≥35 ℃，2 d ≥30 ℃，3 d ≥25 ℃，5 d ≥20 ℃，7 d	每天	顶部和底部为 98%	无
		所有虫种全部虫态（不包括皮蠹类）			≥35 ℃，10 d ≥30 ℃，15 d ≥25 ℃，20 d ≥20 ℃，25 d			
		皮蠹类的全部虫态			≥35 ℃，17 d ≥30 ℃，21 d ≥25 ℃，28 d			

表 2 磷化氢熏蒸最低浓度建议

Table 2 Minimum fumigation recommendations

储藏类型	熏蒸剂	*熏蒸剂量	*熏蒸剂量（有虫粮）	#暴露时间/d	监控间隔期/d	最低应用剂量/(mg/m^3)
气密仓	磷化氢	0.5 g/t 储存量	0.66 g/t 储存量	28	每周，至少在第 7、14 和 21 d 有 3 组数	14 d 时为 100 mg/m^3
气密仓（装载>40%油菜籽，燕麦或豆类）	磷化氢	0.66 g/t 储存量	与粮食管理主管联络	28	同上	14 d 时为 100 mg/m^3
内有防水层仓（所有粮种）	磷化氢	1.5 g/t	与粮食管理主管联络	28	同上	14 d 时为 100 mg/m^3
敞开式舱壁模式	磷化氢	0.75 g/t	1.5 g/t	28	同上	14 d 时为 100 mg/m^3
敞开式舱壁模式（装载有油菜籽，燕麦或豆类）	磷化氢	1.5 g/t	与粮食管理主管联络	28	同上	14 d 时为 100 mg/m^3
筒仓	磷化氢	0.5 g/t 储存量	0.66 g/t 储存量	14	同上	14 d 时为 100 mg/m^3
筒仓（快速熏蒸）	磷化氢	0.5 g/t 储存量	0.66 g/t 储存量	7	每天	350 mg/m^3，持续 7 d
监测：使用经批准的监测设备进行			*只要满足最低剂量要求，剂量就可以变化。			

注：# 在获得粮食管理部门的正式许可后，可以更改暴露时间。

Note: # Exposure period may be varied with formal permission from the Grain Protection Department.

公式

气密仓

剂量×储存量÷500 g（片剂）

剂量×储存量÷1 122 g（带状剂型）

剂量×储存量÷620 g（钢瓶气）

VAPORPHOS 磷化氢钢瓶气

剂量×储存量÷1 000=需要的 kg

增加的剂量（mg/m^3）× S 储存量÷800（用于熏蒸补药）

敞开式舱壁模式

剂量×船舶吨位÷500 g（片剂）

剂量×船舶吨位÷620 g（钢瓶气）

磷化氢

片剂 1.5 kg　　产生 500 g PH_3

带状剂型 3.4 kg　　带状剂型　1 122 g PH_3

G 钢瓶气
含 620 g PH_3
E 钢瓶气
含 300 g PH_3
Vaporphos 钢瓶气
含 22 000 g PH_3

内有防水层仓
剂量×船舶吨位÷ 500 g（片剂）
剂量×船舶吨位÷ 620 g（钢瓶）

SIROFLO（系统）
80 mg/m^3，至少 28 d

（5）在 CBH-Albany 10 000 t 混凝土仓中实验的生物测定结果显示，用 98%氮气处理 2~3 周后，大麦和油菜籽所有样品都没有检测出活虫。对混合虫龄的样品进行培养结果表明，暴露 2~3 周后，赤拟谷盗、米象和谷蠹所有虫态都 100%被控制。处理后的大麦和油菜籽的水分、蛋白质、淀粉、含油量、游离脂肪酸值和种子颜色均没有变化。

（6）CBH 的熏蒸协议规定，谷物储存超 3 个月后必须重新熏蒸。CBH Albany 粮食出口码头现将氮气气调作为一种管理工具，用于港口从上游国家进口的经磷化氢熏蒸过的粮食。从 Albany 出港的粮食因用了氮气气调处理技术，所以最多只用磷化氢处理一次，或者根本不用，只在港口使用氮气气调即可。CBH Albany 粮食出口码头将氮气气调技术作为磷化氢抗性治理的一个管理措施，替代部分磷化氢的使用和控制粮食品质（表 1）。

表 3 惰性气体熏蒸最低建议
Table 3 Minimum fumigation recommendations

储藏类型	熏蒸剂	*熏蒸剂量	*熏蒸剂量（有虫粮）	#暴露时间/d	监控间隔期/d	最低应用剂量/(mg/m^3)
筒仓	氮气	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	按体积计，99%的氮气（1%的氧气），必要情况下要进行补气	成虫，7 d 所有虫态，25 d	每天	顶层氮气浓度为 98% 理想的粮温应为≥20 ℃
筒仓	二氧化碳	按体积计，起始浓度 95%，必要情况下要进行补气	按体积计，起始浓度 95%	最少 14 d	每天	35%，持续 14 d
监测：使用经批准的监测设备进行			*只要满足最低剂量要求，剂量就可以变化			

注：# 在获得粮食管理部门的正式许可后，可以更改暴露时间。
Note: # Exposure period may be varied with formal permission from the Grain Protection Department.

2.2 富氮低氧对粮食品质的影响

使用 FOSS 近红外分析仪对在 25、30 和 35 ℃、99%、98%和 97%氮气的环境下持续处理 4 周的小麦、大麦、燕麦、羽扇豆和油菜籽的水分含量、蛋白质、含油量、淀粉和籽粒颜色进行测定，结果表明这些粮种的这些指标均未受到影响。另外，利用滴定法检测油菜籽在 35 ℃下储存 2 个月期间内的游离脂肪酸，也没有变化。高氮条件下可以抑制油菜籽的呼吸作用，避免出现局部发热，防止高温下导致油料氧化变质。

2.3 基于变压吸附制氮技术的储粮气调系统

（1）最佳充氮方式是立筒仓顶盖关闭后从仓底充气，然后通过连接筒仓顶部空间的管道将气体从地面排出。当排出气体中氮气浓度达到 98%时停止充气。另外，考虑 1%~1.5%的氧气从谷物中解吸需要一天时间，所以需要二次补气，直到排出气体氮气浓度达到 98%为止。

（2）循环利用含有>85%氮气的排出气体可显著节省能源。能将储存环境中的氧气浓度控制在 1%以下是一个很好的结果，这通常是气调的关键点。

3 讨论与结论

尽管气调已经使用了几十年，但澳大利亚是第一个将清洁富氮低氧技术在商业规模筒仓中应用的国家，将其作为磷化氢等熏蒸剂的替代技术，

为农场主和粮食出口行业提供了一种替代性的、价格合理的控制技术，使储存的谷物和油菜籽免受虫害，并处于无化学残留的最佳状态。与我们生测结果类似，Athanassiou 等[6]也发现，通过充氮将氧气浓度降低到 1%，可 100%控制杂拟谷盗所有虫态、可可蛾的卵和幼虫和锯谷盗成虫。我们的研究结果还表明，富氮低氧技术在控制抗磷化氢害虫方面效果显著，这将被视为保护澳大利亚每年 60 亿澳元出口农产品的一个重要进展。Sakka 等[7]在研究在 40 ℃条件下利用 1%O_2的富氮环境处理赤拟谷盗、锯谷盗和米象抗性品系和敏感品系时，也取得了同样的结果。我们的结果表明，随着环境温度的升高，富氮处理的效果增加，这与随着温度的升高害虫代谢活动如呼吸增加有关。Sakka 等[7]也报告了类似的结果，他们发现与 28 ℃相比，在 40 ℃时更易取得 100%的死亡率。

据 Athanassiou 等[8]报道，由于结构易泄漏引起的气密性欠佳，使得氮气在筒仓中的应用很复杂，很难成功。本研究中，来自中国和印度的高效经济氮气制备装置推动了氮气技术的发展，使其适用性更好。从长远来看，按照设备投入和运营成本来算，这项技术只比磷化氢贵一点，目前还没有低氧抗性问题。同时，该系统的成本远低于热处理和其他非化学方法，符合职业健康安全与环境（OHS&E）要求，预计随着时间和应用推广，它将成为用户选择的一个重要特征。

这项技术的重要优势是将油料储存在低氧环境中，能显著抑制呼吸有助于保持质量，因为呼吸过程可能导致局部快速升温发热，高温导致种子氧化变质，保护蛋白质、活力、淀粉、颜色和含油量等关键指标，同时可以防止自燃，避免火灾的风险。

这项技术将进一步提高澳大利亚粮食行业在国内外市场上的声誉。例如，CBH Albany 粮食出口码头现在将氮气气调作为一种管理工具，用于港口进口一些上游国家经磷化氢熏蒸过的粮食，从 Albany 出港的粮食因使用氮气气调处理技术，最多只用磷化氢处理一次，或者无须处理，仅使用氮气气调技术。这项技术为磷化氢抗性的管理提供了解决方案，有可能消除仅依赖一种化学品控制仓储害虫的局面。

致谢：感谢澳大利亚政府合作研究中心（CRC）项目的财政支持。感谢澳大利亚 CRC 对国家植物生物安全研究中心（CRCNPB）、澳大利亚默多克大学和澳大利亚初级产业与区域发展部（DPIRD）的支持。感谢 Pat Collins 博士、David Eagling 博士、Jonathan Banks 博士、Ern Kostas、Greg Hopkins、Matthew Head 和 Chris Newman 在研究和实验方案方面提供的有益建议。感谢 CBH 和 Doug Clarke（西澳大利亚谷物集团，格雷斯湖）在小麦、油菜籽和储存设施采购方面提供的协助。还感谢 Doug 和 Clarke 家族（西澳大利亚谷物集团，Lake Grace）、Ern Kostas、Graeme George、Nicholas Trim 和 Keith Andrews（CBH）协助进行实验。

参考文献：

[1] SOUSA A H, FARONI L R D A, GUEDES R N C, et al. Ozone as a management alternative against phosphine-resistant insect pests of stored products[J]. Journal of Stored Products Research, 2008, 44(4): 379-385.
[2] JAGADEESAN R, NAYAK M K. Phosphine resistance does not confer cross-resistance to sulfuryl fluoride in four major stored grain insect pests[J]. Pest management science, 2017, 73(7): 1391-1401.
[3] AGRAFIOTI P, ATHANASSIOU C G, SUBRAMANYAM B J J O S P R. Efficacy of heat treatment on phosphine resistant and susceptible populations of stored product insects[J]. Journal of Stored Products Research, 2019, 81: 100-106.
[4] NAVARRO S. Modified atmospheres for the control of stored-product insects and mites[M]. HEAPS J W. In insect management for food storage and processing. USA, 2006: 105-146.
[5] ADLER C, CORINTH H G, REICHMUTH C. Modified atmospheres[M]. SUBRAMANYAM B, HAGSTRUM, D.W. In alernatives to pesticides in stored product ipm. USA, 2000: 105-146.
[6] ATHANASSIOU C G, CHIOU A, RUMBOS C I, et al. Effect of nitrogen in combination with elevated temperatures on insects, microbes and organoleptic characteristics of stored currants[J]. Journal of Pest Science, 2017, 90: 557-567.
[7] SAKKA M K, GATZALI F, KARATHANOS V T, et al. Effect of nitrogen on phosphine-susceptible and -resistant populations of stored product insects[J]. Insects, 2020, 11(12): 885.
[8] ATHANASSIOU C G, SAKKA M K. Using nitrogen for the control of stored product insects: One single application for multiple purposes[J]. Agrochemicals, 2022, 1: 22-28. 完

备注：本文的彩色图表可从本刊官网（http//lyspkj.ijournal.cn）、中国知网、万方、维普、超星等数据库下载获取。
英文原文详见 P62-68。

AGARWAL M, NEWMAN J, LI Y Y, et al. Nitrogen as an alternative to phosphine(英文原文)[J]. Science and Technology of Cereals, Oils and Foods, 2024, 32(3): 55-68.

Nitrogen as an Alternative to Phosphine (英文原文)

Manjree AGARWAL[1], James NEWMAN[2], Yan-yu LI[3,4], Li GU[3], Bei-bei LI[3], Yong-lin REN[3]✉

(1. ChemCentre, Government of Western Australia, Perth WA 6102, Australia; 2. CBH Group Australia, Perth WA 6000, Australia; 3. College of Environmental and Life Sciences, Murdoch University, Perth WA 6150, Australia; 4. Institute of Grain Storage and Logistics, Academy of National Food and Strategic Reserves Administration, Beijing 100037, China)

Abstract: The use of nitrogen gas in grain storage has a history of over 30 years. However, it wasn't until the recent emergence of economically efficient pressure swing adsorption (PSA) and membrane separation (MS) nitrogen production equipment that this technology became viable for grain storage. This study first conducted laboratory bioassays over 4, 3, and 2 weeks on wheat, barley, oats, lupin, and canola seeds, exposing them to environments of 25°C, 30°C, and 35°C with nitrogen concentrations of 99%, 98%, and 97%. The study focused on assessing the adult and immature stages of *Trogoderma variabile*, *Tribolium castaneum*, *Rhyzopertha dominica*, and *Sitophilus oryzae*. Subsequently, in-field verification was carried out at the Lake Grace terminal and the Cooperative Bulk Handling (CBH) grain export terminal in Albany, evaluating the efficacy of controlling various storage grain pests and field pests in wheat, barley, and canola seeds, as well as assessing the quality of treated grains. The results showed that pest mortality increased with decreasing oxygen concentration, increasing exposure time, and temperature. However, under low-temperature conditions, nitrogen-rich low-oxygen treatment did not achieve 100% mortality of *Trogoderma variabile* larvae. There was no significant difference in the efficacy of controlling storage pests resistant or sensitive to phosphine. Canola seeds showed better control efficacy compared to other grains. Furthermore, the moisture content, protein, oil content, starch, and grain color quality indicators of various grains were unaffected. A commercially scalable nitrogen-rich low-oxygen application model was successfully developed, providing a solution for controlling pests resistant to phosphine and meeting the growing market demand for insect-free and chemical residue-free grains.

Key words: controlled atmosphere storage; pest management; phosphine resistance; grain quality; application model

Chinese Library Classification Number: TS205

Documentary Identification Code: A **Article ID:** 1007-7561(2024)03-0055-14

Published time on CNKI: 2024-05-13 18:27:37

Published address on CNKI: https://link.cnki.net/urlid/11.3863.ts.20240511.1616.005

Received Date: 2024-02-28

Supported by: the Australian Government’s Cooperative Research Centre Program——Alternatives to Phosphine (No. CRC50147)

Author: Manjree AGARWAL, Female, Doctor, Senior research scientist, Research field: Fumigant and pest control. E-mail: magarwal@chemcentre.wa.gov.au. See more details in PC13

Corresponding author: Yong-lin REN, Male, Doctor, Professor, Research field: Postharvest biosecurity and food safety. E-mail: y.ren@ murdoch.edu.au. See more details in PC8-11

1 INTRODUCTION

The Australian grain industry relies heavily on the internationally accepted treatment of fumigation with phosphine to maintain its harvest free from insect infestation - an important criterion for market access. For a range of sound reasons, phosphine fumigant is the major tool used to control insect infestations in harvested grain. In the past 15~20 years, however, the efficacy of this material is now seriously threatened by the development of resistance in many target pests. The resistance to phosphine in target insect pests has developed to such an extent that it now threatens effective control and, consequently, jeopardises market access. Continued broad-scale use of this fumigant appears to be unsustainable in the long term. There is a need to develop cost-effective, readily adoptable alternatives that will control resistant insects and comply with industry and market standards. At the very least, effective alternatives are needed to reduce selection pressure for resistance and to control resistance outbreaks, while the worst-case scenario is the collapse of phosphine with the need for complete replacement technologies and systems. There is a critical need for the Australian grain industry to research and develop practical, cost-effective replacements for phosphine. Many alternative methods have been evaluated with both advantages and disadvantages [1-3].

The application of modified atmosphere has been long regarded as a promising method for the disinfestation of stored products [4-6]. Nitrogen, carbon dioxide or a mixture there of can be added to grain storages in a controlled fashion to displace or dilute the storage atmosphere. At high concentrations (40% or greater) CO_2 is toxic to insects. Nitrogen is not toxic but is used to displace oxygen to create an atmosphere containing less than 1% oxygen, which is capable of disinfesting stored grain. Nitrogen storage as potential non-chemical alternatives has been recommended as part of a broad phosphine resistance management strategy. Particularly, the phosphine resistance challenge coupled with recent development of pressure-swing absorption (PSA) technology, which can generate large amounts of N_2 relatively inexpensively, has made N_2–based CA a viable proposition. This technology has several advantages over fumigants:

N_2 constitutes 78% of air and air is a rich, free source of N_2;

N_2 is not toxic;

Greatly reduced OHS & Environmental risks;

Provides "organic" and truly residue-free grain;

No known resistance problems;

No reaction with construction materials;

No need for ventilation before grain can be marketed;

No need for product registration.

The project aims to undertake Australia wise national scoping study to develop cost-effective and readily adoptable chemical alternatives using nitrogen-based controlled atmosphere technology to protect and disinfest stored grain. This technology aims to produce insect-free grain at out-turn and control phosphine-resistant insects and has the potential to prolong the useful life of phosphine, complement current management practices and comply with market requirements and environmental and work-place health and safety standards.

The goal is to have nitrogen based controlled atmosphere technology adopted by the collaborating Australian grain companies like CBH, Vitarra and GrainCorp. However, it is likely that once proven other larger storage organizations and growers will adopt the technology.

Field trials of lab-developed protocols will be undertaken using a commercially available pressure swing absorbance N_2 generator, initially on 50 tonne silos (farm scale), and then on 2,500 tonne commercial storages.

2 MATERIALS AND METHODS

2.1 Laboratory evaluation of efficacy of high nitrogen (low oxygen) atmosphere against insect pests and effect on grain quality

2.1.1 Efficacy of high nitrogen (low oxygen) atmosphere against insect pests

The laboratory bioassays were conducted at Murdoch University Post Harvest Plant Biosecurity laboratory. A gas purging flow system (Figure 1) was used to treat the insects with constant concentrations of nitrogen and oxygen and maintain low carbon dioxide concentrations during the period of treatment. Concentrations of nitrogen, oxygen and carbon dioxide were monitored twice a day during the 1~4 weeks treatment period.

The range of nitrogen concentrations were 95%~99% balanced with oxygen for treatment of all stages of *Sitophilus oryzae* (L.), *Tribolium castaneum* (Herbst), *Rhyzopertha dominica* (F.) and

Fig.1 A gas purging flow system was used to treat the insects with constant concentrations of nitrogen and oxygen and maintained low carbon dioxide concentrations during the period of treatment. All 15 cylinders were filled with a known amount (1.8~2 kg) of grain (wheat, barley, oats, lupin and canola). A sealed sachet made of muslin cloth with 40~50 g of mixed age culture of stored grain insects with >200 adults were inserted at a depth of 6 and 23 cm.

Trogoderma variabile (Ballion) in wheat, barley, oats, lupins and canola, and adult stages of Ladybird and Bronzed field beetle (*Adelium brevicorne*) in canola at 20~30 ℃. Bioassay samples were retrieved at the end of the exposure period, the adult insects were counted and removed and the remaining grain incubated at (25±1) ℃ and 65% RH. Subsequent emerging adult insects were counted weekly for a period of 5 weeks, with live and dead adults removed at each count.

a) Laboratory bioassays were conducted on adults of *Trogoderma variabile*, *Tribolium castaneum* and *Rhyzopertha dominica* and *Sitophilus oryzae* in wheat, barley, oats, lupins and canola at 99%, 98% and 97% nitrogen at 25, 30 and 35 ℃ for 4, 3 and 2 weeks exposure period.

b) Laboratory bioassays were conducted on all immature stages of *R. dominica*, *S. oryzae* and *T. castaneum* in wheat, barley, oats, lupins and canola at 99%, 98% and 97% nitrogen, at 25, 30 and 35 ℃ for 4, 3 and 2 weeks exposure period.

c) Bioassays were conducted on all immature stages of *T. variabile* in wheat, barley, oats, lupins and canola 98%~99% nitrogen and at 25, 30 and 35 ℃ for 4, 3 and 2 weeks exposure period.

2.1.2 Efficacy of high nitrogen (low oxygen) atmosphere on grain quality

Samples of wheat, barley, oats, lupins and canola were analysed using a FOSS Infratec, 1 241 Grain Analyzer both before and after exposure to 97%, 98% and 99% nitrogen for period of 1~4 weeks at 25, 30 and 35 ℃.

2.2 Lake Grace farm bin trials

Farm bin-scale trials were conducted on the property of Doug Clarke near Lake Grace (–33.117, 118.607), Western Australia (Figure 2). Nitrogen was applied to wheat and canola held in 75 tonne gas-tight storages ($P^{1/2} \geqslant 180s$) using a pressure swing adsorption (PSA) generator with a capacity of 30 m^3 of 99.5% N_2/hour. Efficacy against insect pests and effect of the storage atmosphere on grain quality were evaluated. The initial trial was conducted on wheat with a temperature of 20 ℃. The final in-store nitrogen concentration was 97%~98%. All adults of *R. dominica*, *S. oryzae*, *T. castaneum* and *Trogoderma variabile* larvae was tested.

A subsequent trial in canola at 35 ℃ at 97% nitrogen was also tested for Bronzed field beetles, Ladybirds and all stages of *R. dominica*, *S. oryzae*, *T. castaneum* and *T. variabile*. Canola seed colour, oil content and levels of free fatty acid was tested during the 2 month storage period using titration method.

Various atmospheric purging methods were evaluated during the trials.

Fig.2 The farm bin-scale nitrogen application trials were conducted at Doug Clarke's farm near Lake Grace (33.117, 118.607), Western Australia. A pressure swing adsorption (PSA) nitrogen generator (capacity of 30 m^3 of 99.5% N_2/hour) was used for purging nitrogen to wheat and canola bines (capacity of 75 tonne).

2.3 CBH Albany grain export terminal trials

A 350 m^3/hour PSA nitrogen generator has been installed at CBH Albany grain export terminal (35°1'50.90"S 117°53'10.54"E). The generator is plumbed to a bank of 10 x 10,000 tonne concrete cells. The project has conducted and completed trials on 5 x 10,000 tonne concrete cells containing newly harvested canola and barley at 30~32 ℃ (Figure 3). The grain was naturally infested with *T. castaneum*, Ladybirds and Bronzed field beetles.

Fig.3 A 350 m^3/hour PSA nitrogen generator has been installed at the CBH Albany grain export terminal (35°1'50.90"S 117°53'10.54"E). The generator is plumbed to a bank of 10 × 10,000 tonne concrete cells.

After 2~3 weeks treatment with 98% nitrogen only, all barley and canola were inspected for export. The bioassay with mixed age cultures of all stages of tested *T. castaneum*, *S. oryzae* and *R. dominica* were conducted along with quality of the treated barley and canola.

3 RESULTS

3.1 Insect response (toxicity) to low O_2/high N_2 concentrations and its relationship to phosphine resistance

a) Laboratory bioassays were conducted on adults and all immature stages of *Trogoderma variabile*, *Tribolium castaneum*, *Rhyzopertha dominica* and *Sitophilus oryzae* in wheat, barley, oats, lupins and canola at 99%, 98% and 97% nitrogen and at 25, 30 and 35 ℃ for 4, 3 and 2 weeks exposure period. The mortality of all stages of all insects tested increased with decreasing levels of oxygen and increasing exposure time and temperature. In comparison with wheat, barley, oats and lupin, in canola high concentrations of nitrogen or low oxygen kills all stages of all tested insects with higher efficacy (Table 2).

Adult stages of Ladybirds and Bronzed field beetles in canola were completely controlled at 95%, 97% and 99% of nitrogen and 25 ℃ for 6, 5 and 3 days exposure period, respectively (Table 1).

Table 1 Recommended dosage of nitrogen and exposure period at different temperatures

Storage Type	Commodity	Insect Species	*Dosage Rate of Nitrogen	*Dosage Rate of Nitrogen (Insect Infested)	Exposure Period of Nitrogen at Different Grain Temperatures	Monitoring Interval (Days)	Minimum Level of Nitrogen Required	Holding Period for outloading
Cells	Canola	All species of adult insect pests	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	⩾35 ℃ & 2 days ⩾30 ℃ & 3 days ⩾25 ℃ & 5 days ⩾20 ℃ & 7 days	Daily	98% in Headspace and bottom	No witholding
		Harvest Beetles and weevils			⩾35 ℃ & 2 days ⩾30 ℃ & 3 days ⩾25 ℃ & 6 days			
		All species of insect pests at all stages (no warehouse beetle present)			⩾30 ℃ & 14 days ⩾20 ℃ & 21 days			
		All stage warehouse beetle			⩾35 ℃ & 14 days ⩾30 ℃ & 18 days ⩾25 ℃ & 25 days			
Cells	Wheat Barley	All species of adult insect pests	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	⩾35 ℃ & 2 days ⩾30 ℃ & 3 days ⩾25 ℃ & 5 days ⩾20 ℃ & 7 days	Daily	98% in Headspace and bottom	No withholding
		All species of insect pests at all stages (no warehouse beetle present)			⩾35 ℃ & 10 days ⩾30 ℃ & 15 days ⩾25 ℃ & 20 days ⩾20 ℃ & 25 days			
		All stage warehouse beetle			⩾35 ℃ & 17 days ⩾30 ℃ & 21 days ⩾25 ℃ & 28 days			

Table 2 Minimum fumigation recommendations

Storage Type	Fumigant	*Dosage Rate of Fumigant	*Dosage Rate of Fumigant (Insect Infested)	#Exposure Period of Fumigant (Days)	Monitoring Interval (Days)	Minimum PPM Required
Sealed Storages	Phosphine	0.5 grams per tonne storage capacity	0.66 grams per tonne storage capacity	28 days	Weekly ideally at 7, 14 & 21 days Minimum 3 Readings	100 ppm at 14 days
Sealed Storage (Containing >40% Canola, Oats or Peas)	Phosphine	0.66 grams per tonne storage capacity	Liaise with Grain Protection Supervisor	28 days	As Above	100 ppm at 14 days
Internal Tarping (All commodities)	Phosphine	1.5 grams per tonne	Liaise with Grain Protection Supervisor	28 days	As Above	100 ppm at 14 days
Open Bulkheads	Phosphine	0.75 grams per tonne	1.5 grams per tonne	28 days	As Above	100 ppm at 14 days
Open Bulkheads (Containing canola, oats or peas)	Phosphine	1.5 grams per tonne	Liaise with Grain Protection Supervisor	28 days	As Above	100 ppm at 14 days
Cells	Phosphine	0.5 grams per tonne storage capacity	0.66 grams per tonne storage capacity	14 days	As Above	100 ppm at 14 days
Cells (Rapid Fumigation)	Phosphine	0.5 grams per tonne storage capacity	0.66 grams per tonne storage capacity	7 days	Daily	350 ppm for 7 days
Monitoring: To be carried out using approved monitoring equipment.			*Dosage rate can be varied providing minimum PPM requirements are met.			

Exposure period may be varied with formal permission from the Grain Protection Department.

FORMULAE

SEALED STORAGE

Dosage Rate × Storage Capacity ÷ 500 gms (Tablets)
Dosage Rate × Storage Capacity ÷ 1122 gms (Blankets)
Dosage Rate × Storage Capacity ÷ 620 gms (Cylinders)

OPEN BULKHEAD

Dosage Rate × Tonnage ÷ 500 gms (Tablets)
Dosage Rate × Tonnage ÷ 620 gms (Cylinders)
G Cylinders contains 620 gm PH_3
E Cylinders contains 300 gm PH_3
Vaporphos cylinder contains 22000 gms PH_3

INTERNAL TARPING

Dosage Rate × Tonnage ÷ 500 gms (Tablets)
Dosage Rate × Tonnage ÷ 620 gms (Cylinders)

SIROFLO

80 ppm for min 28 days

VAPORPHOS

Dosage Rate × Storage Capacity÷ 1000 = kg required
PPM Increase × Storage Capacity÷ 800 (for fumigation top up)

PHOSPHINE

Tablets 1.5 kg evolves 500 gm PH_3
Blankets 3.4 kg evolves 1122 gm PH_3

b) Laboratory bioassays show that there is no difference in mortality under nitrogen treatment between phosphine-resistant and susceptible strains of adults and all immature stages of *R. dominica*, *S. oryzae*, *T. castaneum* and *T. variabile*.

c) In Lake grace farm bin trial with PSA generator, all adults of *R. dominica*, *S. oryzae* and *T. castaneum* were killed after one week and complete extinction of all life stages occurred after 3 weeks exposure at 20 ℃ with 97%~98%, but 6%~10% of *Trogoderma variabile* larvae survived.

d) A subsequent trial in Lake grace farm bin trial with PSA generator in canola at 35 ℃ showed that with 7 days exposure to nitrogen at 97% all Bronzed field beetles and Ladybirds were eliminated, and after 2 weeks exposure all stages of *R. dominica*, *S. oryzae*, *T. castaneum* and *T. variabile* were killed. Canola seed colour, oil content and levels of free fatty acid did not change during the 2 months storage period.

e) Bioassay results of CBH Albany trials in 10,000 tonnes concrete cells showed no live insects after 2~3 weeks treatment with 98% nitrogen, for all barley and canola samples. The bioassay with mixed age cultures show that all stages of tested *T. castaneum*, *S. oryzae* and *R. dominica* were killed after 2~3 weeks exposure. The treated barley and canola had no change in moisture content, protein, starch, oil content and level of free fatty acid and seed colour.

f) CBH's fumigation protocols state that grain must be re-fumigated after 3 months storage. CBH Albany grain export terminal now incorporate the use of nitrogen as a management tool for grain coming in from up country that has been treated with Phosphine. This means that effectively all grain exported from Albany will only be treated with Phosphine once, or not at all, with the use of nitrogen only at port. The introduction of Nitrogen at CBH Albany grain export terminal has offered solutions for management of phosphine resistance an alternative to phosphine treatment and a grain quality control method (Table 1).

3.2 Knowledge of the effects of low O_2/high N_2 concentrations on grain quality

There was no effect of nitrogen on moisture content, protein, oil content, starch and seed colour of wheat, barley, oats, lupin and canola at 97%, 98% and 99% for period of 1~4 weeks at 25, 30 and 35 ℃ using FOSS Infratec. In addition, free fatty acids tested in canola using titration method also showed no change during the 2 months storage period at 35 ℃. Canola stored under high N_2 maintained quality by inhibiting the respiration process that can lead to rapid localised heating and prevented the oxidation that leads to seed deterioration at this high temperature.

Table 3 Minimum fumigation recommendations

Storage Type	Fumigant	*Dosage Rate of Fumigant	*Dosage Rate of Fumigant (Insect Infested)	#Exposure Period of Fumigant (Days)	Monitoring Interval (Days)	Minimum PPM Required
Cells	Nitrogen	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	99% Nitrogen (1% Oxygen) by volume to be topped up as necessary	Adult Insects 7 Days All Life Stages 25 Days	Daily	98% in Headspace Ideally ≥ 20 C Grain Temp
Cells	Carbon Dioxide	95% initial concentration by volume to be topped up as necessary	95% Initial concentration by volume	Minimum 14 days	Daily	35% @ 14 Days
Monitoring: To be carried out using approved monitoring equipment.			*Dosage rate can be varied to help achieve minimum PPM requirements.			

Exposure period may be varied with permission from Grain Protection Department.

3.3 Nitrogen-based controlled atmosphere grain storage system using pressure-swing absorbtion technology

a) The most efficient method to purge nitrogen was through the base of the bin with the top lid closed and air purging from the silo through a pipe connected to the headspace, exiting at ground level. The exhaust air was measured until it reached 98% nitrogen. After one day, 1%~1.5% oxygen was desorbed from grain, requiring the storage to be topped up with nitrogen until the exhaust air again contained 98% nitrogen.

b) A recirculation technique can reuse the exhausted air contained >85% nitrogen with significant savings in energy. In addition, oxygen levels were maintained less than1% at the base of storage – an excellent result as this is normally the weak point for controlled atmosphere technology.

4 DISCUSSION AND CONCLUSION

Although controlled atmosphere storage has been in use for decades, Australia has become the first country to successfully develop clean high nitrogen/low oxygen technology at commercial scale silos as an alternative to fumigants such as phosphine. The technology offers an alternative, affordably priced control technology to growers and the grain export industry to keep stored cereal grains and canola free from pests and in peak condition without chemical residues. Similar to our bioassay results, Athanassiou et al.[6] have also found that the application of nitrogen to reduce the oxygen level to 1% was lethal for all life stages of the confused flour beetle, eggs and larvae of the cacao moth, and adults of the sawthoothed grain beetle. Our results have also shown that nitrogen is equally effective in controlling phosphine resistance pests, which is seen as an important advance in helping to shield Australian rural exports worth $6 billion a year. Sakka et al.[7] results also show that both phosphine-resistant and susceptible populations of the *T.castaneum*, *O. surinamensis*, and S. *oryzae* (L.) in commercial nitrogen chambers exposed to 1% O_2 at 40 ℃.

Our results show that as we increase the temperature the effectiveness of nitrogen treatment increase. This can be attributed to increase in metabolic activity like respiration with increase in temperature. Similar results were reported by Sakka et al.[7] who reported that 100% mortality was observed at 40 ℃ compared to 28 ℃.

Athanassiou et al.[8]have reported that the application of nitrogen in silos is complicated because of the leaky structure and this technology cannot be successful unless the silos are gas tight. In our study, the use of high efficient and low-cost nitrogen generators from China and India has given nitrogen technology a boost and made this a much more practical technology. Including capital and operating costs the technology is only a little more expensive in the long term than using phosphine – but without the added issues of insect resistance. The system is of considerably lower cost than heat disinfestation and other non-chemical methods, meets OHS&E requirements and it is expected that over time will become a significant feature of buyer preferences.

An important advantage of this technology is that all the key aspects of grain quality, protein, viablity, starch, colour and oil content – are preserved in a nitrogen atmosphere. Storing oilseeds in a low oxygen atmosphere prevents the risk of self generated heat and fire. This storage process of canola significantly contributed to maintaining quality by inhibiting the respiration process that can lead to rapid localised heating and prevented the oxidation that leads to seed deterioration at this high temperature.

This technology will significantly contribute to further enhance the Australian grain industry reputation on the domestic and international market. For example, the CBH Albany grain export terminal now incorporates the use of nitrogen as a management tool for grain coming in from up country that has been treated with Phosphine. It is projected that all grain exported from Albany will only be treated with Phosphine once, or not at all, using only nitrogen. This technique has offered solutions for management of phosphine resistance potentially removing a reliance on only one chemical for control of storage pests.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the Australian Government’s Cooperative Research Centres Program (CRC). The support from the Australia CRC for National Plant Biosecurity (CRCNPB), Murdoch University, Australia and the Department of Primary Industries and Regional Development (DPIRD), Australia is gratefully acknowledged. We thank Dr Pat Collins, Dr David Eagling, Dr Jonathan Banks, Ern Kostas, Greg Hopkins, Matthew Head and Chris Newman for their helpful advice on research and trial protocols. We thank CBH and Doug Clarke (Western Australia Grains Group, Lake Grace) for their assistance with the procurement of wheat, canola and storage facilities. We thank also Doug and the Clarke family (Western Australia Grains Group, Lake Grace), Ern Kostas, Graeme George, Nicholas Trim and Keith Andrews (CBH) for assistance in the conduct of the trials.

REFERENCES

See in its Chinese version P61. 完