研究简报

# 磷矿浮选剂 S-808 及其尾矿水对鱼类和胚胎的毒性

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S-808 是我国选矿科技工作者研制的一种新型磷矿浮选剂．湖北省荆襄磷矿矿务局王集矿，在选矿过程中采用 S-808 作为抑制剂直接浮选中低品位钙质磷块岩，获得特殊的选矿效果．为此化工部矿山局委托我们开展磷矿浮选剂 S-808 对鱼类的毒性和毒理学的研究．

## 一、材料和方法

S-808 是由湖北省荆襄磷矿矿务局王集矿选矿厂提供的工业品（纯度为 56%），呈黑色块状物．经蒸馏水溶解后呈酸性，用 $Na_2CO_3$ 调 pH 至 7 左右，配制的母液浓度 1ml ≈ 10 mg，配好的母液贮放于冰箱内备用．用等对数间距设计若干个浓度的试验组，并设置对照组，做二个平行试验．

试验用的草鱼受精卵是由水生所试验养殖场提供．取回的受精卵待其发育到原肠早期，在解剖镜下逐一挑选发育正常的胚胎进行毒性试验．每个试验容器内投放 50 个草鱼胚胎；草鱼为 15 尾；孔雀鱼苗为 10 尾．

试验容器：草鱼胚胎和草鱼苗的毒性试验，采用直径为 12cm、高为 6cm 的玻璃结晶皿，盛试液 400ml．孔雀鱼苗的试验亦采用上述规格的玻璃结晶皿．

试验期间的水温，草鱼胚胎毒性试验是在 27±1℃；草鱼苗的试验在 23—24.5℃；孔雀鱼苗的试验是在 21.5—23℃．

试验用的稀释水是武昌东湖水厂的自来水，经活性炭过滤，静置 24 小时以上．其水质情况：pH 7.54；电导率（μs/cm）200；总硬度 2.1mg/L（以 $CaCO_3$ 计）；酚酞碱度 1.7 mg/L（以 $CaCO_3$ 计）．

毒性试验采用半静态式．试验期间的试液溶解氧均保持在 5mg/L 以上．试验步骤基本按《美国污水和工业废水标准检验法》[1]进行．

试验时间：胚胎试验是孵化后再继续饲养到受精后的第十天，此时已渡过了一段认为对毒物最敏感的时期——卵黄吸收耗尽时期．鱼苗试验的时间是 96 小时．

## 二、试验结果

1. 以死亡率为指标

**表1　草鱼胚胎发育到游泳期的死亡率[1)]**

| 浓度(mg/L) | 对照 | 0.18 | 0.56 | 1.0 | 3.2 | 5.6 | 10.0 |
|---|---|---|---|---|---|---|---|
| 死亡率(%) | 1 | 1 | 1 | 1 | 1 | 17 | 37 |

1) 死亡率：(死亡数/试验总数)×100%

由表 1 中可见，用死亡作为观察指标，浓度在 3.2mg/L 以下，在草鱼的胚胎发育过程中没有出现高于对照组的死亡率．浓度高于

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5.6 mg/L 的试验组，对草鱼的胚胎发育有明显的影响，死亡率显著升高。

2. 以畸形为指标

**表 2　草鱼胚胎发育至游泳期的畸形率**

| 浓度 (mg/L) | 对照 | 0.18 | 0.56 | 1.0 | 3.2 | 5.6 | 10.0 |
|---|---|---|---|---|---|---|---|
| 畸形率(%) | 0 | 0 | 0 | 6.6 | 27.4 | 60 | 95 |

$EC_{50} = 3.816$ mg/L

95% 的可信限　3.287—4.118mg/L

回归方程　$y = 3.023x + 3.242$

由表 2 中可见，0.56 mg/L 以下的浓度没有产生畸形，即为无影响的最高浓度，在 1mg/L 以上的浓度可以观察到各种不同类型的畸形胚胎，而且畸形率与试验浓度呈现正

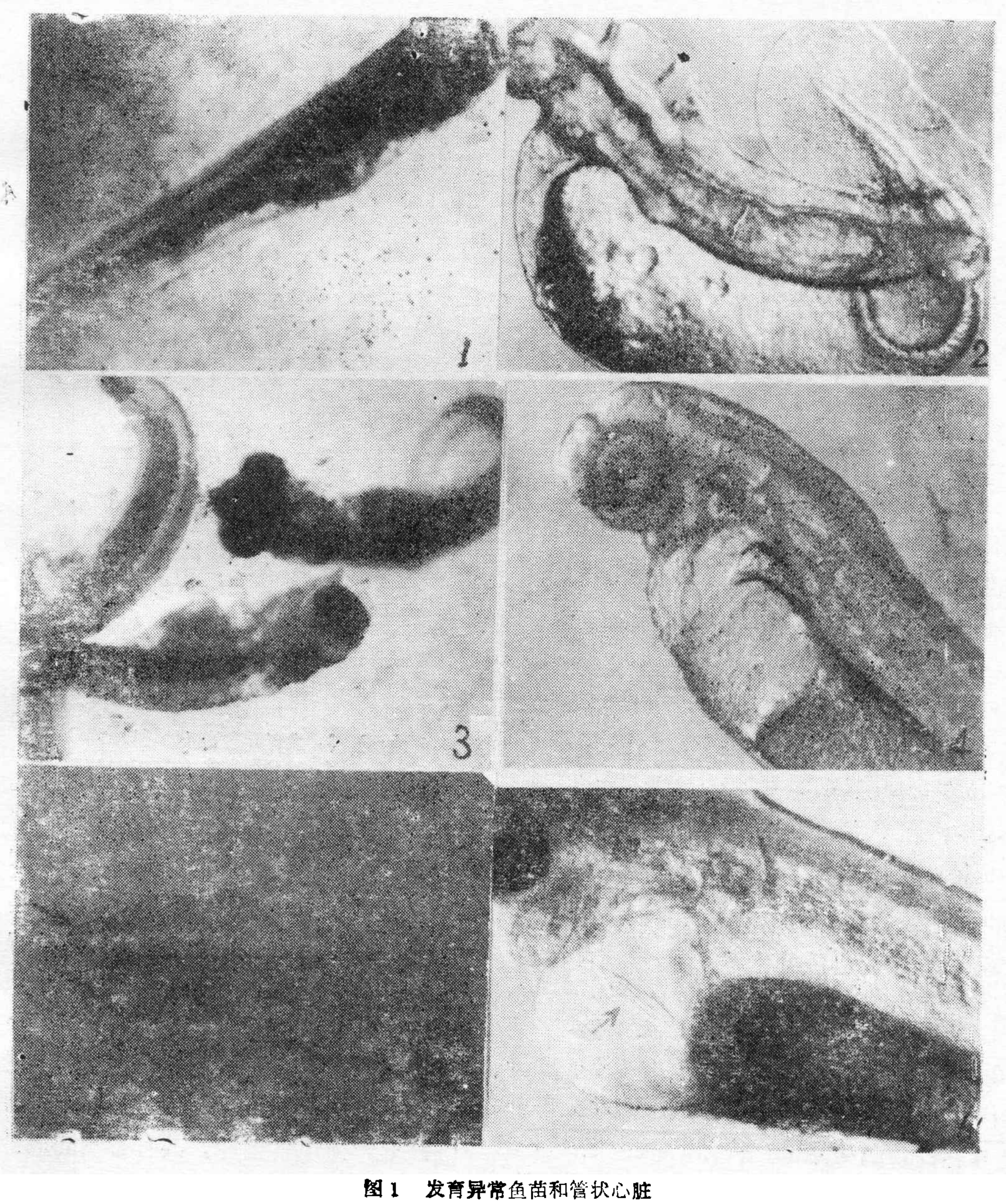


**图 1　发育异常鱼苗和管状心脏**

1. 正常草鱼苗　2. 草鱼苗尾鳍上翻 (5.6 ppm)　3. 草鱼苗弯体畸形 (5.6 ppm)　4. 发育正常的心脏　5. 脊索在尾部产生膨大物(箭头所示，5.6ppm)　6. 心脏发育不全，形成管状心脏(箭头所示，5.6ppm)

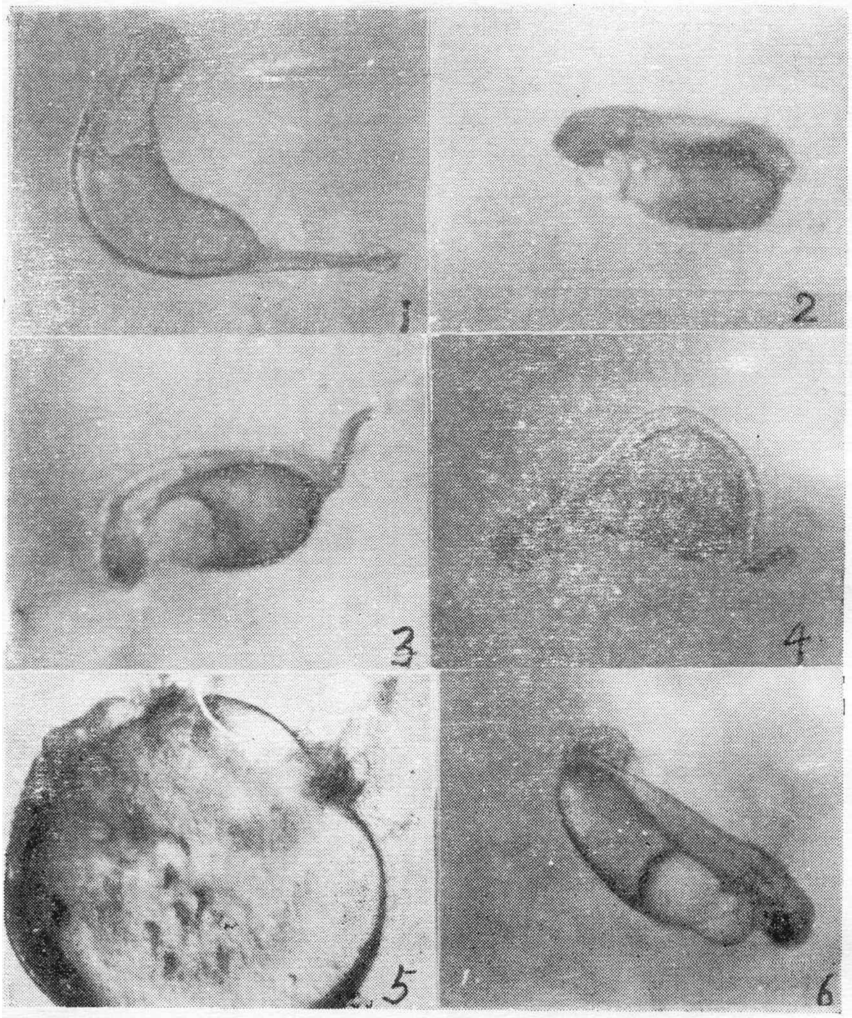


图2　发育异常鱼胚胎

1. 发育正常的胚 胎(5.6 ppm)　2.发育异常胚胎 (5.6 ppm)　3. 发育异常的胚胎 (10ppm)
4. 发育异常胚胎 (7.5ppm)　5.未分化的胚胎 (5.6 ppm)　6. 尾鳍膜卷曲 (10 ppm)

相关.

畸形出现的类型有：胚胎弯体；未分化胚；尾鳍膜不展，有的还出现卷曲；尾鳍处出现数个泡状物；心脏分化不完善，形成管状心脏(图1和图2)。

3. 草鱼胚胎10日存活率试验

表3　草鱼胚胎10日存活率

| 浓度 (mg/L) | 对照 | 0.18 | 0.56 | 1.0 | 3.2 | 5.6 | 10.0 |
|---|---|---|---|---|---|---|---|
| 10日存活率(%) | 99 | 98 | 97 | 90 | 64 | 24 | 0 |
| 10日死亡率(%) | 1 | 2 | 3 | 10 | 36 | 76 | 100 |

求得10日的 $LC_{50}$ = 3.694mg/L

95% 的可信限　3.030—4.503mg/L

回归方程　$y = 2.038x + 3.843$

在胚胎的毒性试验过程中，用96小时很难求得 $LC_{50}$ 值，因此试验延迟到第十天才结束，这样求得10日的 $LC_{50}$ 值为3.694mg/L。由表3中还可以清楚地看到，有影响的浓度基本上仍然是 1mg/L 以上的浓度，这与以畸形作为观察指标，其有影响的最低浓度(1mg/L) 是一致的。

4. 鱼苗的毒性试验

（1）草鱼苗毒性试验

**表 4　草鱼苗的 96 小时的死亡率**

| 浓度（mg/L） | 对照 | 10 | 18 | 24 | 32 |
|---|---|---|---|---|---|
| 死亡率(%) | 0 | 0 | 50 | 100 | 100 |

在毒性试验过程中实测到96小时的 $LC_{50}$ 值是 18mg/L。

（2）孔雀鱼苗的毒性试验

**表 5　孔雀鱼苗 96 小时的死亡率**

| 浓度（mg/L） | 对照 | 10 | 32 | 56 | 75 | 100 |
|---|---|---|---|---|---|---|
| 死亡率(%) | 0 | 0 | 40 | 100 | 100 | 100 |

试验结果用直线内插法求得孔雀鱼苗96小时的 $LC_{50}$ 值为 35mg/L。

## 三、讨　论

1. 由试验结果表明，工业品 S-808 对草鱼苗的 96 小时的 $LC_{50}$ 值为 18mg/L；对孔雀鱼苗的 96 小时的 $LC_{50}$ 值为 35mg/L。可是在草鱼的胚胎毒性试验中求得10日的 $LC_{50}$ 值为 3.694 mg/L。试验浓度在 1mg/L 就出现畸形，畸形率与试验浓度呈现正相关。出现畸形的类型有：胚体弯曲（弯体），鸡形胚，未分化胚，尾鳍膜不展，有的在尾鳍处出现1—3 个泡状物；心脏分化不完善，形成管状心脏，围心腔膨大等。因此工业品 S-808 对鱼类胚胎的毒性较高，并可能会有致畸作用。

2. 在 S-808 的胚胎毒性试验中，以死亡作为观察指标，试验浓度 5.6 mg/L 则为有影响的最低浓度，而以畸形作为观察指标，其有影响的最低浓度为 1mg/L，它们的浓度之比是 5.6 倍，所以在鱼类的胚胎毒性试验中，以畸形作为观察指标则更为敏感些。原来建议以 10mg/L 为地面水安全浓度*，由此看来对鱼类胚胎是不安全的，而且在 10 日的胚胎毒性试验中，10mg/L 浓度组全部死亡，无一例存活。因此 S-808 以 10mg/L 浓度为地面水的安全浓度，这个建议有必要重新考虑修改。

3. 本试验求得的草鱼苗对 S-808 的 96 小时的 $LC_{50}$ 值为 18mg/L，而 1978 年我们曾做过的 S-808 对白鲢鱼种的毒性试验，求得的 96 小时的 $LC_{50}$ 值为 110mg/L，这要比本试验求得的 18 mg/L 高得多。其原因，一方面是所用的试验生物材料的敏感性有差异，另一个原因是 1978 年用的 S-808 是矿山化工设计院提供的，样品为黑色糊状物，本试验所采用的是荆襄磷矿矿务局王集矿选矿厂提供的黑色块状物，其剂型不相同。因此根据这次试验结果的鉴定，S-808 工业品对鱼类的毒性应修正为“毒级”[4]。

## 参 考 文 献


[1] 吴鹏鸣译，工业废水处理利用文集（第一辑），289—310 页，中国工业出版社，1956 年。
[2] 尹伊伟等，中国环境科学，**6**(2)，3—7(1986)。
[3] 张甫英、尹伊伟，鱼类学论文集（第五辑），153—158 页，科学出版社，1986 年。
[4] Joint IMCO-FAO-UNESCO-WMO Group of Experts on the Scientific Aspects of Marine Pollution, Abstract of the Reports of the Firsr Session, *Water Res.*, **3** (7), 995—1005 (1969).


（收稿日期：1987 年 8 月 18 日）

* S-808 毒性鉴定会资料，1982 年 5 月。

· 环境信息 ·

# 远东的水生羊齿植物（Azolla）能去除废水中的有毒金属

以色列希伯莱大学农业系的一位专家发现 Azolla 可用来提取镉、铬、铜、镍、铀和锌。这些金属最后把 Azolla 毒死。将这些已富集金属致死的植物收割；晒干备提取这些金属用。这种工艺的专利权掌握在 Yissum 研究开发公司手中。这位专家和他的植物学家同事们是在筛选可以大量生产作为牲畜饲料的植物时发现 Azolla 有吸收富集金属的能力的。

张　良　摘译自 *ES&T*，**21**(12)，1145(1987)。

The experimantal results show that under the conditions of carbon monoxide below 200 ppm within 16 hours of chambering time, there is no obvious injury on leaves of woody plants. But the ratio of photosynthesis is varied from different biocharacters of woody plants. When 100 ppm CO pollution, the relation of ratio of photosynthesis and the chambering time is exponential function, and $P_t/P_o=5.75$ exp (0.001t) to *Fraxinus chinensis* and $P_t/P_o=7.04$ exp (1.9 10t) to *Puruns davidiana*. (See pp. 27—29)

**Injuries to Tree Leaves by Simulated Acid Rain and Resistant Nature of the Trees**

*Zhang Jiawu, Feng Zongwei et al.* (Institute of Applied Ecology, Academia Sinica, Shenyang)

The paper gives a general description of the effects of simulated acid rain on tree leaves. The experiments have been done in Hunan Experimental Station of Forest Ecology. After the simulated acid rain were sprayed upon tree leaves, there appeared some symptoms: discoloration of greens, tissue necrosis, dewatering and early withering. And injurious extents on leaves were fundamentally due to the rain acidity, duration of spraying and conditions of sunlight and temperature. However, because of different tissue structures of the tree leaves, their resistant capacity were varied. (Sea pp. 30—33)

**Toxicity of Floatation Agent S-808 of Phosphatic Ore and Mineral Wastewater to Fishes and Embryos**

*Zhang Fuying and Yin Yiwa* (Institute of Hydrobiology, Academia Sinica, Wuhan)

Toxic test determining larvae of grass carp and guppy for 96-hour $LC_{50}$ was 18 mg/L and 35 mg/L respectively, 10-day $LC_{50}$ of grass carp embryo was 3.69 mg/L. For fish embryos in 1 mg/L, there appeared deformation. Deformation percentage and concentration were of positive correlation. In fish toxic test, deformed index was more sensitive than dead index. The toxic test showed that, according to classfication standard, S-808 was a "poisonous grade" of fish toxicity. S-808 in floating process was treated with physiochemical method and toxicity of dressing mineral wastewater decreased, so the value of $LC_{50}$ in the test could not be determined, and there didn't appear deformation of fishes. (See pp. 34—37)

**Tests on the Residues of 5% *Bestox* in Cotton Fields**

*Zhou Hou'an et al.* (Institute of Zoology, Academia Sinica, Beijing)

Experiments on the residual kinetics of *Bestox* emulsion (5%) were carried out in the cotton fields. The results showed that the half-life of *Bostox* emulsion (5%) was 23 to 25 days in soil, and 3 to 5 days on leaves. The residues were not observed in cotton seeds even by using dosages 1.5 to 2.0 times of the conventional ones. *Bestox* is low toxic to mammals and there is no systemic action. The results can give a reliable basis for rationalizing the use of *Bestox* in the cotton field and limting MRL value in cotton seeds. (See pp. 38—41)

**Ascertainment of Main Factors for Biological Denitrification System Using Orthogonal Test**

*Du Shelin et al.* (Institute of Environmental Pretection, Shanghai Petrochemical Complex, Shanghai)

Hydraulic retention time (HRT), ratio of the volume of anaerobic tank to the volume of aerobic tank (I: R) and reflux ratio (r) have been established as three main factors in a biological denitrification system by using mathematically the orthogonal test method of Lg ($3^4$). Thus, in such a system for the treatment of a combined wastewater containing nitriles and sodium thiocyanate in high concentration, it was determined that HRT, I: R and r are 24 hours, 1:3 and 5.5 respectively, and they would be more favourable process parameters. In addition, an analysis of the whole system is made in this paper. (See pp. 42—46)

**Removal of Mercury from Wastewater with Maize-Starch Dregs**

*Liu Manying and Kang Weijun* (Hobei Medical College, Shijiazhuang, Hobei Province)

This paper deals with removal of mercury from wastewater by using maize-starch dregs. The experimental result shows that the rate of removal is 99.9%, and Saturated capacity is 45 mg/g. The method seems to be a cheap and efficient one for treating mercury-contained liquids. (See pp. 47—48)

**Method for Determination of Twelve Phthalate Esters in Natural Water**

*Kang Junxing* (Research Center for Eco-Environmental Sciences, Academia Sinica, Beijing) *Hing-biu Lee* (National Water Research Institute, Canada Center for Inland Waters)

An Analytical method was developed and validated, which permits determination parts per billion levels of twelve phthalate esters in natural water. Water sample was extracted with methylene chloride, and the extract was cleaned up by using silica gel liquid chromatographic column prior to determination of the phthalate esters by capillary column ECD-GC, (See pp. 49—54)

**Spectrophotometric Determination of Trace Beryllium in Water and Wastewater after Adsorption concentration by Activated Carbon**

*Qiu Xingchu, Cheng Jun and Zhu Yingquan* Ganzhou Institute of Environmental Science, Ganzhou, Jiangxi Province)

In this paper the optimum conditions of colour reaction of Be-CAS-CPC and adsorption concentration by activated carbon has been studied. In the buffer solution of urotropine pH 5.0. The adsorption maximum of the complex is near 605 nm. Beer's law is obeyed for 0-0.70 g *Be*/25ml (2cm cell) ranges. It is applied to determine the trace Be in Water by spectrophotometric method, which is simple exact and rapid. (See pp. 55—58)