

余氯对水生生物的影响

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摘要: 氯是滨河、滨海企业冷却水常用的防治污损生物的处理剂。总结近年来国内外氯在企业冷却水中的应用、氯对浮游植物、浮游动物、贝类、鱼类等影响的研究成果, 为制定冷却水余氯排放标准和水产养殖的合理布局提供了参考, 针对我国大量滨海电厂即将建立的现状, 分析了余氯研究在中国海域研究的不足, 提出了氯对我国海洋生物影响不同层面的研究方向。认为氯对生物种群的毒性, 氯对生物群落组成、结构和生态演替的影响, 以及减轻或避免余氯污染的对策是需要进一步解决的科学问题。

关键词: 余氯; 水生生物; 热(核)电厂; 生物污损

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Advanced in effect of residual chlorine on hydrobios

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Abstract: Chlorination is widely used for preventing biofouling in power plant cooling water systems. Recent research has indicated that chlorine sourced from the cooling water of power plant is one of the major harmful factors which damage adjacent water ecosystem. In this paper, the technology and research progress on the utilization of chlorine in the cooling water of enterprises and harmful effects of the residual chlorine on phytoplankton, zooplankton, fish and shellfish, etc. were reviewed.

Though 0.2 mg L⁻¹ chlorine may kill 60%~80% unicellular algae, phytoplankton biomass could be recovered after 3~5 days, but the species composition would be changed.

Zooplankton is more sensitive to chlorine than phytoplankton. When it is exposed to the chlorine, and the lethal concentration 50% is lower in continuously filling of the chlorine than in intermittent way.

The effect of chlorine on shellfish is more complicated than other animals, it varies with the various species, ages, chlorine concentration, temperature, and season alteration, but except for *Brachidontes striatulus*.

Regarding finfish, chlorine exposure would lead to gill damage, but some confused results have been reported, e. g. minnows could acclimate to chlorine, and the avoidance reaction of *Brevoortia tyrannus* colony to chlorine is more superior than that of its individual, however, the mechanism of these phenomena is still unclear.

As references, data and viewpoints from various documents are significant for stipulating for drainage standard of residual

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chlorine in cooling water, and the rational distribution of aquiculture. Up to date, however, no research on toxicity of chlorine to most marine species has been done in China, and as a result, there is not any criterion for judging marine ecological security, when many large power plants are constructed in the coast.

The author considers that in the future studies on the toxicity of chlorine to marine populations, the effect of chlorine on species composition, community structure and ecological succession, as well as the countermeasures for avoiding or lightening pollution of the residual chlorine should be focused on.

Key words: residual chlorine; hydrobios; ecosystem; power plant

滨河、滨海电厂和企业生产通常采用附近的自然水体作为冷却水,冷却系统在运行过程中会出现水生生物附着生长。这一现象被称为生物污损(biofouling)^[1]。生物污损可分为两类:一类是由贻贝、藤壶和水螅虫等大型生物引起的管道系统和排水渠的阻塞;另一类是由细菌和真菌等微生物生长形成的生物膜^[2,3]。两类生物污损相互联系,生物膜是大型生物附着的基础^[2],两者都可导致热传输效率降低,给企业运行带来不良影响。美国早在 1924 年便采用氯进行电厂污损生物的控制^[4],20 世纪 40 年代开始,加氯和生产废水的余氯对水域自然生态的负面影响逐渐为国外学者所关注,Turner^[5]研究了氯对海水管道中附着生物的影响。之后,不同研究者陆续在余氯对水域生产力的影响^[6,7]、余氯对水生生物的毒性及毒性机理^[3,8~12]、不同形态余氯的毒性差异^[13]、余氯和温升对水生生物交互作用^[14~18]等方面进行了广泛研究。而我国关于余氯对水生生物影响研究起步较晚^[19~22],至今还没有冷却水余氯排放标准。

本文旨在综述国内外的研究成果,并对今后的研究重点进行展望,同时为我国以自然水为冷却用水的企业确定水体加氯浓度和制定冷却水余氯排放标准提供科学依据。

1 氯在企业冷却水中的应用

滨河、滨海企业冷却系统的主要防污针对的是软体动物的幼体^[16,23]。连续向海水中加低浓度氯($0.1 \sim 0.5 \text{ mg L}^{-1}$)便可阻止翡翠贻贝幼体在冷却系统内的附着^[24]。氯对多形饰贝(*Dreissena polymorpha*)^[17]和紫贻贝(*Mytilus edulis*)^[25]的幼虫毒性实验则表明 0.1 mg L^{-1} 的余氯就会引起幼虫死亡。因此,企业日常运行一般采用低剂量氯来防治贻贝等生物附着^[16],这一剂量通常低于 1 mg L^{-1} ^[25],或低于 0.2 mg L^{-1} ^[24],甚至更低,为 0.1 mg L^{-1} ^[15,26]。

为了降低生产成本和减少对水生生态的影响,企业经常采用间歇通氯的方式防止污损生物在冷却系统中的附着,但有时却不能奏效^[24,27]。Rajagopal 等^[24]报道 Madras 核电厂从 1976 年开始对冷却水采用间歇通氯进行附着生物的控制,该厂冷却水排放口余氯浓度控制在 $1 \sim 2 \text{ mg L}^{-1}$,持续 1 h,偶然持续 8 h,1987 年调查却发现该厂冷却系统中污损生物量为 $35 \sim 211 \text{ kg m}^{-2}$ 。Rajagopal 等^[27]指出,对于食物丰富的环境,每天通氯几小时或者每月通氯几天,即使采用高浓度($3 \sim 5 \text{ mg L}^{-1}$)也不能杀死贻贝,原因在于当加氯处理时贻贝外壳闭合,而停止加氯后 7~15 min 便能恢复进食;对于食物贫乏的环境,相同浓度的余氯却会因营养限制的原因可以很好的控制贻贝的生长。对多形饰贝、*Mytilopsis leucophaeata*、紫贻贝进一步研究发现,连续通氯使受试贝类达到 100% 死亡的同期内,间歇通氯(通 4 h,停 4 h)只有 0~5% 死亡^[27]。

氯对冷却水中水生生物致毒的主要因素是余氯浓度水平和作用时间,同时还受水体温度、盐度、pH 和有机质的影响^[27,28]。余氯和热的共同作用可以导致斑马贻贝(zebra mussel)的死亡提前,如驯化温度为 $20 \sim 25 \text{ }^{\circ}\text{C}$,无氯 $30 \text{ }^{\circ}\text{C}$ 条件下斑马贻贝死亡 95% 的时间为 842 h,而 0.5 mg L^{-1} 余氯 $30 \text{ }^{\circ}\text{C}$ 条件下该时间仅为 32.8 h,死亡时间缩短大约 95%^[18]。

Saravanane^[29]从余氯对海洋浮游植物生物量影响的角度分析,认为余氯本身对海域造成的影响很微弱。因为 1) 氯在处理冷却水过程中,与其他因素协同作用于水生生物,这些因素包括温升、水泵中的剪切力、冲刷作用、压力剧变等;2) 海水运动对余氯排放区域有强稀释作用;3) 由氯产生的残余氧化剂在海水中的衰减很快,这一衰减由水体需氯量、有机物卤化、卤化物降解等化学衰减过程构成。

实际上,由于氯元素性质活泼,其在自然水体中多以 -1 价离子态存在。因此,人为增加的 0 价或 $+1$ 价余氯必然会对水生生物产生影响。

2 余氯对水生生物的影响

海洋生态系统是一个动态系统,许多食物网交错存在,其中任何一个种群发生变化都可能导致其他生物种群的巨大变化^[29]。

2.1 余氯对浮游植物的影响

电厂温排水中的余氯是损害浮游植物的主要因素,而温排水的热冲击对浮游植物的影响不大^[30]。 0.2 mg L^{-1} 的氯可以直接杀死冷却水中 60%~80% 的藻类^[31]。

但 Glasstone 等^[32]认为即使 20% 的浮游植物种群被杀死,水域的净影响也可以被忽略。Hamilton 等^[30]按氯处理时损失

91%的浮游植物,氯处理时间占一天的 25%,冷却用水占河流流量的 30%,则对美国马里兰州 Patuxent 河畔 Chalk Point 电厂邻近水域浮游植物受氯处理的损失估算结果仅为 6.6%。Sarvanane 等^[29]在海滨电厂排水口有效氯浓度控制在 0.2~0.5 mg L⁻¹时,将取水口、冷却管内、排水口的 3 份水样进行室内培养,硅藻的初始浓度分别为 413、352、381 ind/ml,达到同一细胞密度(6.7×10⁴~8.3×10⁴ ind/ml)分别需要 3、6、8d,说明浮游植物具有较强的恢复潜能,余氯对浮游植物的损伤能得到较快恢复。但恢复后的浮游植物种类组成发生变化,如电厂取水口、冷却管内、排水口水样的藻类培养试验表明透明海链藻(*Thalassiosira hyalina*)在培养初期所占比例与其他浮游植物接近,但在冷却管内和排水口水样的培养后期却成为优势种,优势度达到 100%。

此外,不同水质条件下,氯对浮游植物的影响程度不一。当海水中总颗粒物和溶解有机碳占比例较高时,则同样浓度的氯对浮游植物的影响较小,因为大量氯主要被前者所消耗^[7,29]。

2.2 余氯对浮游动物的影响

浮游动物虽是水生生态系统的重要组成部分,但目前对浮游动物受氯的影响研究报道较少(见表 1)。从表 1 可见,浮游动物对氯较敏感,较低浓度的氯即可对浮游动物产生明显的影响;浮游动物受氯连续暴露影响的浓度低于间歇暴露的浓度。

表 1 余氯对浮游动物的影响^①
Table 1 Effect of residual chlorine to various zooplankton

物种 Species	温度 Temperature (C)	盐度 Salinity	判定指标 Criterion	影响浓度 Effect concentration(mg L ⁻¹)	参考文献 Reference
大型 蕨 <i>Daphnia magna</i>	25±1	淡水 freshwater	48-h <i>LC</i> ₅₀ ^②	0.032	[3]
	25±1	淡水 freshwater	48-h <i>ILC</i> ₅₀ ^③	0.055 ^④	[3]
	16	淡水 freshwater	24-h <i>LC</i> ₅₀	0.038	[19]
	19	淡水 freshwater	24-h <i>LC</i> ₅₀	0.047	[19]
	25	淡水 freshwater	24-h <i>LC</i> ₅₀	0.043	[19]
<i>Hyalella azteca</i>	25±1	淡水 freshwater	96-h <i>LC</i> ₅₀	0.078	[3]
	25±1	淡水 freshwater	96-h <i>ILC</i> ₅₀	0.301 ^④	[3]
<i>Mysidopsis bahia</i>	25±1	20	96-h <i>LC</i> ₅₀	0.062(0.052~0.074)	[3]
	25±1	20	96-h <i>ILC</i> ₅₀	0.210(0.169~0.257) ^④	[3]
	25±1	20	<i>LC</i> ₅₀	0.073	[12]
	25±1	20	96-h <i>ILC</i> ₅₀	0.267 ^⑤	[12]
<i>Neomysis</i> sp.	15	28	<i>LC</i> ₅₀	0.162	[33]

①未作说明均为连续通氯 Unmarked organisms were tested for continuous exposures;②*LC*₅₀:连续暴露的半数致死浓度 The concentration resulting in 50% of the test organisms lethal for continuous exposures;③*ILC*₅₀:间歇暴露的半数致死浓度 The concentration resulting in 50% of the test organisms lethal for intermittent exposures;④每隔 8h 通氯气 40 min Organisms were exposed intermittently to a dilution series of oxidant for 40 min every 8 h;⑤每隔 2h 通氯气 40min Organisms were exposed intermittently to a dilution series of oxidant for 40 min every 2 h

2.3 余氯对贝类的影响

余氯可造成贝类滤食率、足活动频率、外壳开闭频率、耗氧量、足丝分泌量、排粪量等亚致死参数的降低,从而使贝类失去附着能力^[8,28,34~37]。当余氯浓度低于 1 mg L⁻¹时,贝类仍可以打开外壳进行摄食,但摄食速率降低^[36];浓度更高时,贝类便被迫关闭外壳,依靠体内积蓄的能量和缺氧呼吸作用生存,直至能量完全消耗或代谢废物达到毒害水平^[23,36]。

Masilamoni 等^[28]认为余氯对贝类致毒的机理可能为:(1)氯直接对贝类鳃上皮细胞造成伤害;(2)由氯造成的氧化作用破坏贝类呼吸膜,导致其体内缺氧、窒息而死;(3)氯直接参加贝类酶系统的氧化作用。

余氯对贝类的影响存在物种间差异。Lewis^[23]报道称紫贻贝经 4.43 mg L⁻¹余氯处理 49 h,放回原海水中可在 30 min 内恢复活动。Rajagopal 等^[36]报道 0.75 mg L⁻¹的余氯是条纹短齿蛤(*Brachidontes striatulus*)生理功能受到影响的临界值,条纹短齿蛤甚至对 0.25 mg L⁻¹的低浓度余氯也能作出滤食率降低 6%~30%的反应。翡翠贻贝(*Perna viridis*)对余氯非常敏感(<0.15 mg L⁻¹)^[28]。斑马贻贝甚至可以感知 0.04 mg L⁻¹的余氯作用,并立即作出关闭外壳的反应^[38]。Rajagopal^[27,37]研究发现,紫贻贝、翡翠贻贝、股贻贝(*Perna perna*)、条纹短齿蛤、变化短齿蛤(*Brachidontes variabilis*)和菲律宾偏顶蛤(*Modiolus philippinarum*)用氯处理时,达到 100%死亡率的时间存在较大差异,1 mg·L⁻¹余氯作用下,受试个体全部死亡的时间介于 288 h 和 1104 h 之间,紫贻贝最长,变化短齿蛤最短。

余氯对贝类的影响存在体龄差异。*M. leucophaeata* 的余氯毒性试验表明,0.25 mg L⁻¹余氯作用下,其 2 mm 个体全部死亡

的时间为 89d,而 10 mm 个体全部死亡的时间为 109 d^[27]。但变化短齿蛤的个体大小对氯的响应没有显著性差异^[37]。

余氯对贝类的影响存在温度差异。Jenner 等^[16]报道翡翠贻贝在 0.5 mg L⁻¹余氯作用下,30℃时达到 95%死亡率的时间是 1d,而在 34℃时,这一时间仅为 1h。Rajagopal 等^[39]报道 *M. leucophaeta* 在 0.5 mg L⁻¹余氯作用下,5℃时达到 95%死亡率的时间为 99d,30℃时则为 47d。斑马贻贝^[15,17]也有同样的趋势。

余氯对贝类的影响存在浓度差异。同一种贝类,余氯浓度越高,则其死亡时间越短^[9,28,36,40]。

余氯对贝类的影响存在季节差异。Jenner^[15]研究发现多形饰贝受相同浓度余氯作用时,春季和夏季全部死亡的时间不同。Rajagopal 等^[39]用采自 6 月(夏季)和 11 月(冬季)的 *M. leucophaeta*,经 20℃驯化 2 周后,用 1,2mg L⁻¹和 3 mg L⁻¹氯进行毒性试验,均发现该贝非养殖季节(11 月~翌年 4 月)比养殖季节(6~10 月)对氯的忍耐性强。

余氯对贝类的影响研究结果列于表 2。

表 2 余氯对贝类的影响^①

Table 2 Effect of total residual chlorine to various mussel species

物种 Species	总余氯 ^② (mg L ⁻¹)	温度 Temperature (℃)	持续时间 Duration	死亡率 Mortality (%)	参考文献 Reference
紫贻贝 <i>Mytilus edulis</i>	1.00	—	39 d	100	[9]
	10.00	—	7 d	100	[9]
	4.43	16.6	20 d	100	[23]
	1.00	20	966 h	100	[27]
翡翠贻贝 <i>Perna viridis</i>	1.00	29~30	34 d	100	[40]
	5.00	29~30	5 d	100	[40]
	0.5	30	1 d	95	[16]
	0.5	34	1 h	95	[16]
	0.72	30.4~31.0	588 h	100	[28]
	9.7	30.4~31.0	4 d	100	[28]
	1.00	29.1	34 d	100	[37]
	1.00	29~30	14 d	100	[26]
变化短齿蛤 <i>Brachidontes variabilis</i>	1.00	29.1	260 h	100	[37]
条纹短齿蛤 <i>Brachidontes striatulus</i>	1.00	29~30	24 d	100	[36]
	2.00	29~30	15 d	100	[36]
	3.00	29~30	10 d	100	[36]
偏顶蛤 <i>Modiolus modiolus</i>	1.00	29~30	11 d	100	[26]
多形饰贝 <i>Dreissena polymorpha</i>	0.4	春季 Spring	> 3 weeks	100	[15]
	0.4	夏季 Summer	2 weeks	100	[15]
	0.25	12~15	21 d	90	[38]
	0.50	12~15	19 d	93	[38]
	1.00	12~15	17 d	93	[38]
	0.50	18~21	9 d	100	[11]
	0.50	17~27	9 d	100	[41]
	1.00	20~22	20 d	80	[13]
	2.50	20~22	13 d	100	[13]
	5.00	20~22	7 d	100	[13]
	1.00	20	588 h	100	[27]
	2.00	20.1	18.5 d	100	[39]
	1.00	—	23 d	95	[42]
	1.00	20	36 d	100	[35]
	2.50	20	15 d	100	[35]
<i>Mytilopsis leucophaeta</i>	5.00	20	15 d	100	[35]
	10.00	20	36 d	100	[35]
	0.5	5	99 d	95	[39]
	0.5	30	47 d	95	[39]
	1.00	20	1104 h	100	[27]

① 所有生物均为连续暴露试验 All organisms were tested for continuous exposures;② Total residual chlorine

2.4 余氯对鱼类的影响

余氯对鱼鳃有损伤作用,使鱼鳃组织发生病变,如组织增生、上皮组织脱离、鳃中积累大量粘液、生成动脉瘤等,从而影响并

阻碍鱼鳃与水中溶解氧的交换^[43,44]。余氯也可能通过鱼鳃组织渗入血液中,把血液中能携带氧的还原性血红蛋白氧化成不能携带氧的正铁血红蛋白,还可能抑制正铁血红蛋白还原性酶的活性,从而导致血液运载氧的能力下降^[45]。表 3 为文献中报道的余氯对鱼类的影响结果。

有些鱼类可以通过自身的调节,对氯产生一定的抗性,提高自身对氯的忍耐力^[10,46]。如 Lotts 等^[46]认为 0.04~0.08 mg L⁻¹的余氯可以引发鲤科鱼对氯的适应能力,但这一适应过程中鱼类生理和生化方面的变化并不清楚。令人奇怪的是,鱼类群体比鱼类个体对氯更敏感,如大西洋油鲱(*Brevoortia tyrannus*)群体对余氯的回避反应比个体强^[14]。

表 3 余氯对鱼类的影响^①
Table 3 Effect of residual chlorine to various fish

物种 Species	来源 Source	鱼龄 Age(d)	判定指标 Criterion	影响浓度 Effect concentration mg L ⁻¹	参考文献 Reference
虹鳉 <i>Oncorhynchus mykiss</i>	淡水 freshwater	15	96-h LC_{50} ^②	0.059 (0.050~0.071)	[3]
金体美鲮 <i>Notemigonus crysoleucas</i>	淡水 Freshwater	幼鱼 Young	96-h LC_{50}	0.304 (0.255~0.358)	[3]
斑鲮 <i>Ictalurus punctatus</i>	淡水 Freshwater	—	100%急性死亡 ^③	0.24~0.30	[44]
白鲢 <i>Hypophthalmichthys molitrix</i>	淡水 Freshwater	幼鱼 Young	回避反应 Avoiding reaction	0.15~0.20	[19]
条纹石鲈 <i>Morone saxatilis</i>	半咸水 Brackish water	22	96-h LC_{50}	0.14	[47]
		60	96-h LC_{50}	0.19	[47]
		388	96-h LC_{50}	0.23	[47]
月银汉鱼 <i>Menidia beryllina</i>	咸水 Saltwater	11	96-h ILC_{50} ^④	0.193 (0.149~0.241) ^⑤	[3]
		—	96-h ILC_{50}	0.227 ^⑥	[12]
		—	LC_{50}	0.128	[12]
		—	96-h LC_{50}	0.143 (0.115~0.183)	[3]
大西洋月银汉鱼 <i>Menidia menidia</i>	—	—	96-h LC_{50}	0.037	[48]
<i>Menidia peninsulae</i>	—	—	96-h LC_{50}	0.054	[49]
大西洋油鲱 <i>Brevoortia tyrannus</i>	海水 Seawater	—	强回避反应 ^⑦	0.10~0.15	[14]
平鲷 <i>Rhabdosargus sarba</i>	海水 Seawater	幼鱼 Young	48-h LC_{50}	0.19 (0.16~0.22)	[22]
黑鲷 <i>Sparus macrocephalus</i>	海水 Seawater	幼鱼 Young	48-h LC_{50}	0.18 (0.15~0.22)	[22]

①未作说明均为连续通氯 Unmarked organisms were tested for continuous exposures;② LC_{50} :连续暴露的半数致死浓度 The concentration resulting in 50% of the test organisms lethal for continuous exposures;③100% acute death;④ ILC_{50} :间歇暴露的半数致死浓度 The concentration resulting in 50% of the test organisms lethal for intermittent exposures;⑤每隔 8h 通氯气 40 min Organisms were exposed intermittently to a dilution series of oxidant for 40 min every 8 h;⑥每隔 2h 通氯气 40min Organisms were exposed intermittently to a dilution series of oxidant for 40 min every 2 h;⑦Intensive avoiding reaction

3 总结与展望

氯气凭借其广谱性、价格低廉、来源方便、使用简便等特点,被广泛用作生物防污的化学试剂^[16]。但不同物种对氯的忍受性存在差异,而我国氯对许多海洋物种的毒性研究资料却很少;加之掌握生物杀伤剂对目标生物的致死毒性和亚致死毒性的准确信息对于研制合适的生物杀伤剂非常重要^[16]。因此,有必要针对我国不同区域的污损生物开展氯忍耐力研究,为有效控制污损生物提供科学的理论依据。

尹伊伟等^[19]就氯对我国淡水水生生物的毒性已作了详细的研究,为我国制定淡水渔业水质标准提供了科学依据。但随着近年来许多大型火电厂和核电厂都将建在经济发达的海滨(河口或港湾),冷却水的余氯自然会对海域生态和养殖环境产生一定负面影响。如养殖鱼类受网箱等限制,不能逃离氯污染区域。因此,为了充分利用海水资源和兼顾保护海域生态的平衡,就必需限制工业冷却水余氯的排放浓度,给定一个允许标准,而该标准又必须以主要经济生物及其他水生生物的最大耐受浓度值为依据。因此,针对我国不同海区的主要经济生物开展氯的影响研究具有重要现实意义。

从经济学和环境安全的角度考虑,必须对余氯影响下水生生物种群的响应有一个恰当的认识^[3,39]。但余氯对不同浮游植物种类的影响以及对浮游植物生物量的研究报道都很少。如果氯的影响足以改变水生生物群落的组成结构,就会导致物种多样性降低、生态系统异源演替、乃至关键种丧失,甚至可能导致生态系统退化。因此,开展氯对生物群落的组成、结构和生态演替的影

响具有重大生态学意义。

冷却水排放中余氯的影响可以通过源头控制来降低。通过改进系统设计,或者在生产中采用更有效的系统管理和经营方式,都可以降低氯气和其他生物杀伤剂的用量。设计冷却系统的工业解决方案中,可以采用钛金属代替铜合金作热交换系统的防腐蚀材料,增加输水系统表面光滑度、提高水流速度都可以降低系统受到生物污损的可能性。如可以采用效率更高的隔栅和过滤设施使进入系统的碎屑最小化,结合海绵球过滤系统,对系统管道增加硅酮涂层等措施来降低污损生物的附着^[50]。

此外,氯气与自然水体中有机质、 NH_4^+ 等反应生成多种具有毒性的副产物^[2],基于环境友好的角度,污损生物防治的高新技术研究还在继续进行^[16,51],并在生产实践中发展了许多替代生物防污技术。如采用 ClO_2 、 Br_2 、优氯净、二氯异氰尿酸钠、异噻唑啉酮、30% Tallow 1,3-丙二胺、氨丙烷等具有表面活性的生物杀伤剂^[50,52]。顾继东等^[51]则发现从斑马贻贝体内分离的细菌及其体外代谢物可用防止斑马贻贝的附着。但这些技术的成本或者高于氯气,或者离实际应用还有很长距离,因此新型低价长效生物防污剂的研制仍是今后研究的重点。

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