Current situation for lead-free copper alloys in Japanese drinking water applications and Field test results of lead leaching into drinking water

Research & Development
Sambo Plant
Mitsubishi Shindoh Co., LTD
Sakai, Osaka, Japan

Agenda

1. **Current situation toward lead-free in Japan**

2. **Field test results of lead leaching in actual environment**

Current situation toward lead-free in Japan-1

■Drinking water standard for lead was tightened in April 2003

Start of actual lead-free trend in drinking water applications

☆Lead-free has been realized mainly for water meters , valves and fittings

→ ・Newly-installed water meters must be lead-free

・Lead-free water meters to reach approx. 50% penetration in 2009

☆Lead-free being accelerated for faucets;

Surface treatment still popular to reduce lead leaching

■Lead-free progressing in Automobile/Electric applications

■Standardization of lead-free copper alloys in Japan

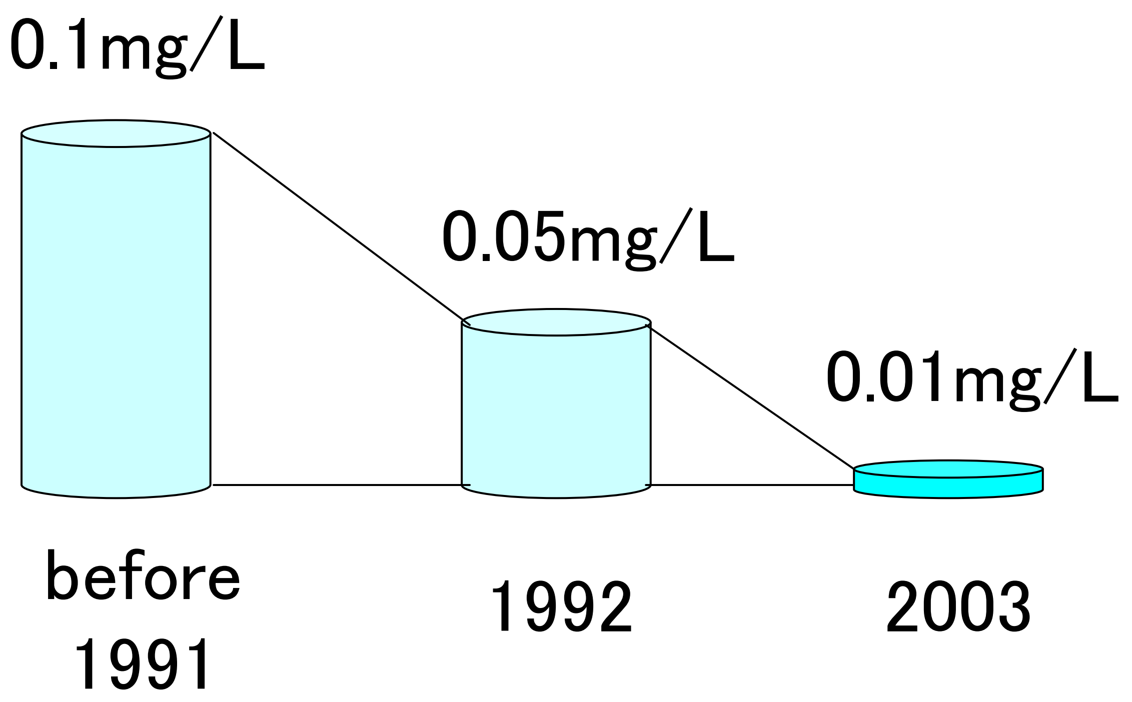
2005 Industry standard JCBA T204 for wrought copper

2006 Registration as JIS H2202, 5120, 5121 for castings

Current situation toward lead-free in Japan-2

1. In line with the trend of using lead-free copper alloys for waterworks applications in Japan, bismuth-bearing copper alloy and silicon-bearing copper alloy have been used. These alloys are used for both castings and rods, showing a higher consumption for the former. Bismuth-bearing copper alloy are used more than silicon-bearing copper alloy in terms of weight.
2. For forged products and machined products, either silicon-bearing copper alloy or bismuth-bearing copper alloy is selected depending on the requirements of the final specifications.
3. Both silicon-bearing copper alloy and bismuth-bearing copper alloy products have been produced in amounts well exceeding 10,000 tons on an accumulated basis in the seven years since the start of full-scale mass production. Meanwhile, no problem has been reported in the market.
4. While the ingot cost of bismuth is expensive (approx. US$26,000/ton※), its percentage in the brass alloy is as low as 2% at the most. Therefore, the cost efficiency should not be reviewed solely from the ingot cost, when giving consideration to the fact that the copper content should be increased by 10% or slightly more in the silicon-bearing copper alloy with an ordinary brass ingot.
   ※:Average in 2008, Metal cost of copper : approx. US$7,000/ton in 2008
5. Reviewing the availability aspect, in recent years it has often been difficult to procure copper metal or recycled copper material. On the other hand, the stable procurement of silicon and bismuth ingots has never been at risk.

Lead
Water Quality Standards



Equipment for water supply service

Test methods of effect to water quality (JIS S 3200-7:2004)

Substance	End feed water implements (Faucets etc.)	Feed water pipe
Copper and its compounds	0.1(0.98) mg/L or less	1.0 mg/L or less
Zinc and its compounds	0.1(0.97) mg/L or less	1.0 mg/L or less
Cadmium and its compounds	0.001 mg/L or less	0.01 mg/L or less
Lead and its compounds	0.001(0.007)mg/L or less	0.01 mg/L or less
Arsenic and its compounds	0.001 mg/L or less	0.01 mg/L or less
Selenium and its compounds	0.001 mg/L or less	0.01 mg/L or less
Chromium(VI) compounds	0.005 mg/L or less	0.05 mg/L or less
Mercury and its compounds	0.00005 mg/L or less	0.0005mg/L or less
Aluminum and its compounds	0.02 mg/L or less	0.2 mg/L or less
Iron and its compounds	0.03 mg/L or less	0.3 mg/L or less
Magnesium and its compounds	0.005 mg/L or less	0.05 mg/L or less

Test methods of water quality in Japan

Leachate (to make 1L)	pH:7.0±0.1 (Adjust by using HCl or NaOH) Hardness:45±5mg/L Alkalinity:35±5mg/L Residual chlorine:0.3±0.1mg/L 1mL of NaClO(Available chlorine:0.3mg/mL) + 22.5mL of 0.04M $NaHCO_3$ + 11.3mL of 0.04M $CaCl_2$
Conditioning	14days; Use the leachate of about 23℃
Leaching	16hours; Fill, seal the inside of equipment under test with the leachate of about 23℃
Correction of analysis result	$\rho_B = NF \times C'$ $NF = SAF/SAL \times VL/VF$ ρ_B =correction value(mg/L), NF=correction factor, C'=analysis result, SAF, SAL=contact surface area of in contact with drinking water, the leachate respectively VL, VF=internal volume in contact with the leachate, drinking water respectively

Composition of lead-free copper alloy castings on JIS H5120 (Copper and Copper alloy castings)

Alloy No.	Principal Composition								
	Cu	Sn	Zn	Bi	Se	P	Si	Pb※1	Production※2 ton/month
CAC804	74.0～78.0	—	18.5～22.5	—	—	0.05～0.2	2.7～3.4	0.25	100
CAC901	86.0～90.6	4.0～6.0	4.0～8.0	0.4～1.0	—	—	—	0.25	1300
CAC902	84.5～90.0	4.0～6.0	4.0～8.0	1.0～2.5	—	—	—	0.25	
CAC903B	83.5～88.5	4.0～6.0	4.0～8.0	2.5～3.5	—	—	—	0.25	
CAC911	83.0～90.6	3.5～6.0	4.0～9.0	0.8～2.5	0.1～0.5	—	—	0.25	

※1 Maximum allowance composition

※2 Average in 2008

Lead-less free-cutting alloy rods and bars

Composition of lead-free copper alloy rods and bars on JCBA (Japan Copper and Brass Association) T204

Alloy No.	Cu	Bi	Si	Pb	Zn	Sn	P	Fe	Cd	Se+Al+Sb +Te+Ni	Other	Production※1 ton/month
C6801	57.0～64.0	0.5～4.0	–	≦0.01	rem.	0.1～2.5	≦0.2	≦0.5	≦0.0075	–		250
C6802	57.0～64.0	0.5～4.0	–	≦0.1	rem.	0.1～3.0	≦0.2	≦0.7	≦0.0075	–		
C6803	57.0～64.0	0.5～4.0	–	≦0.01	rem.	0.1～2.5	≦0.2	≦0.5	≦0.0075	0.02～0.6		
C6804	57.0～64.0	0.5～4.0	–	≦0.1	rem.	0.1～3.0	≦0.2	≦0.7	≦0.0075	0.02～0.6		
C6932	74.0～78.0	–	2.7～3.4	≦0.10	rem.	≦0.6	0.05～0.2	≦0.1	≦0.0075	–	Mn≦0.1 Ni≦0.2	100

※1 Average in 2008

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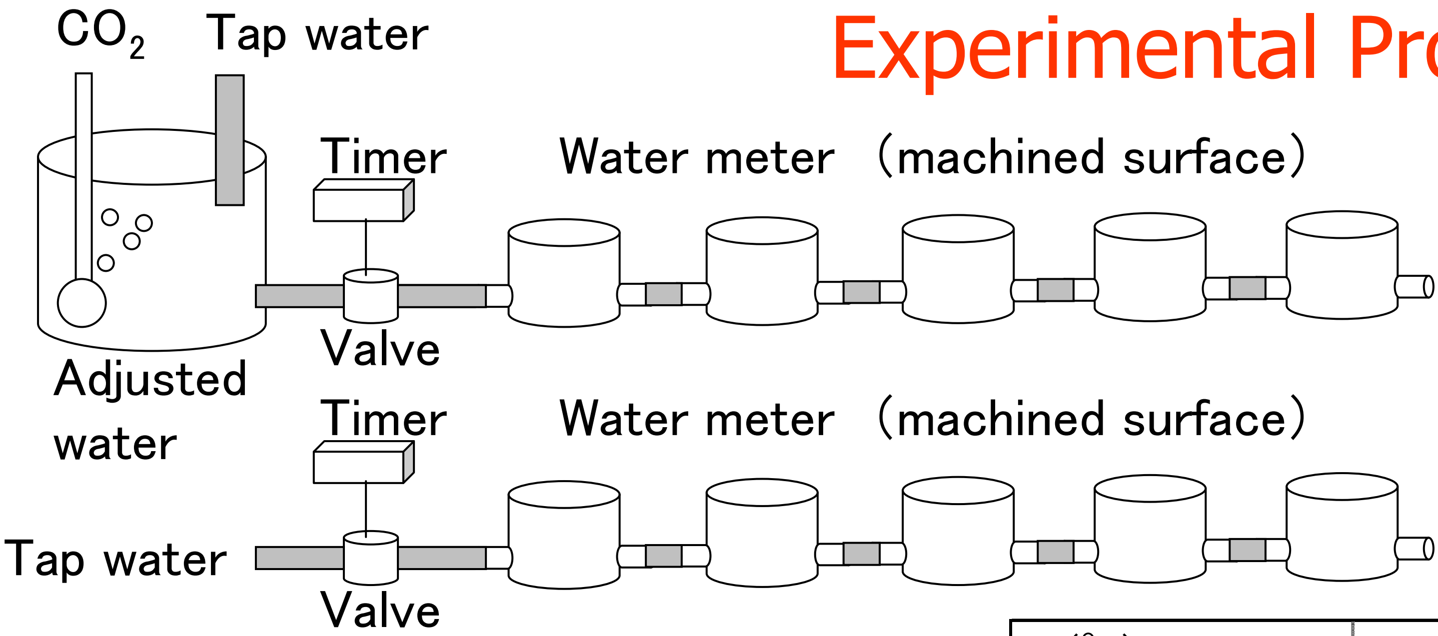
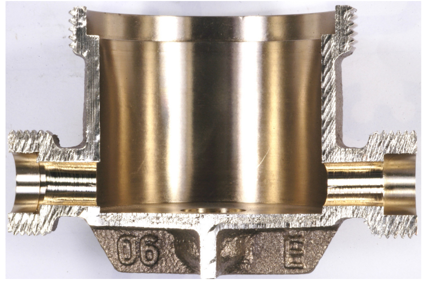
Lead leaching test into tap water in Japan

Chemical composition of specimens

Alloys		Cu	Pb	Sn	Si	Zn
Leaded brass		59.41	3.16	0.29	—	rem.
Lead-free alloy		75.89	0.02	0.01	3.15	rem.
Leaded red brass	no treatment	83.11	5.93	4.04	—	rem.
	surface treatment	84.92	5.52	4.27	—	rem.

Experimental Procedure





13mm bore Water meter

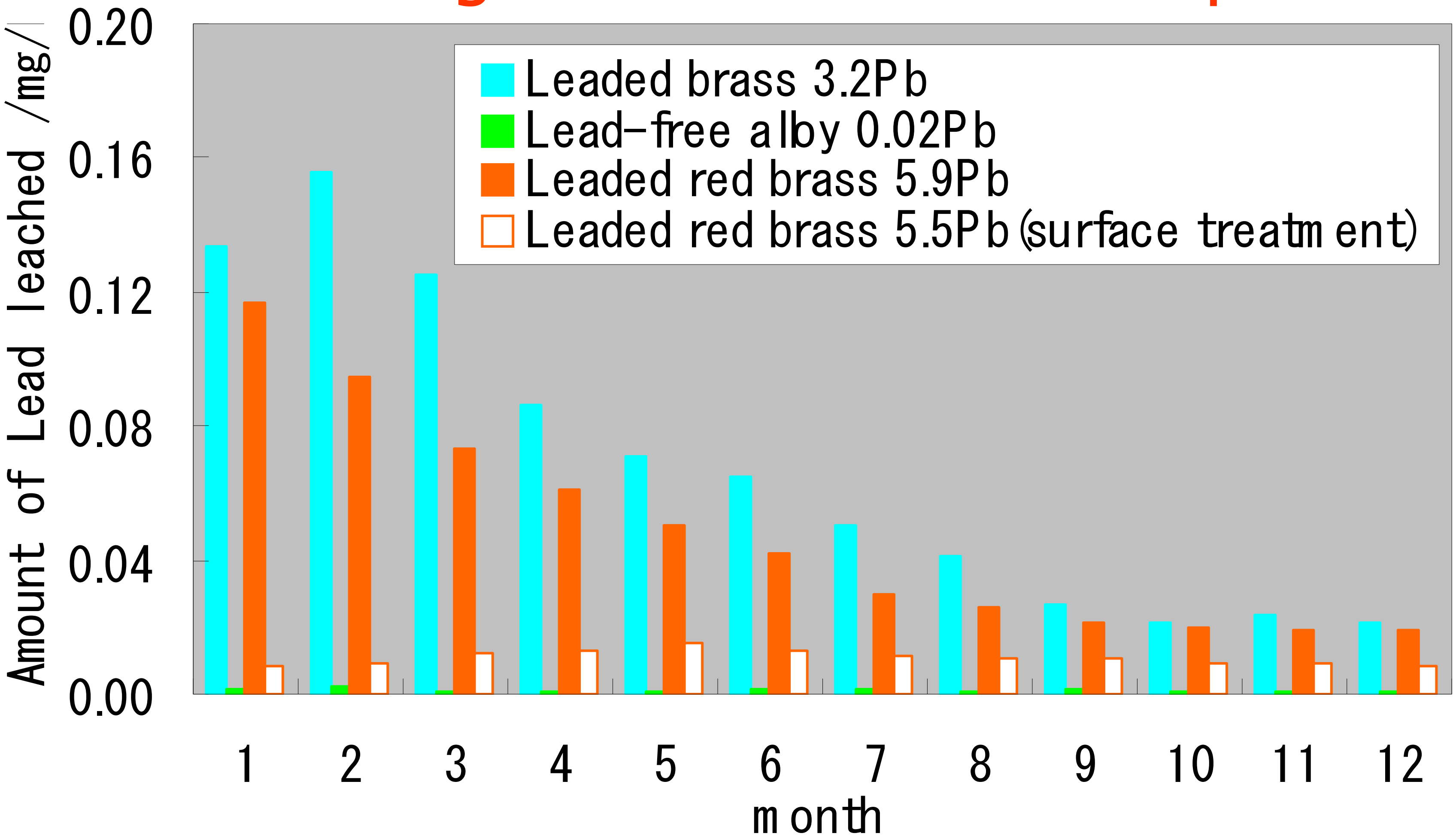
Contact area : $6dm^2$
Content volume : 390mL
Flow cycle : pass 0.5hour
(at room temp.) stagnation 7.5hours
Test Water : pH 7.3±0.2
CO_2 adjusted water
pH 6.8±0.2

Leaded brass rod was machined to have the same parameters as the water meter.

pH (℃)	7.3 (18.3)
total alkalinity	48
total residue	160
free carbon dioxide	2.7
bicarbonate	59
residual chlorine	0.3
Ca	20
Pb	<0.001
Cu	0.01
Zn	<0.01
Langelier's index	−1.3

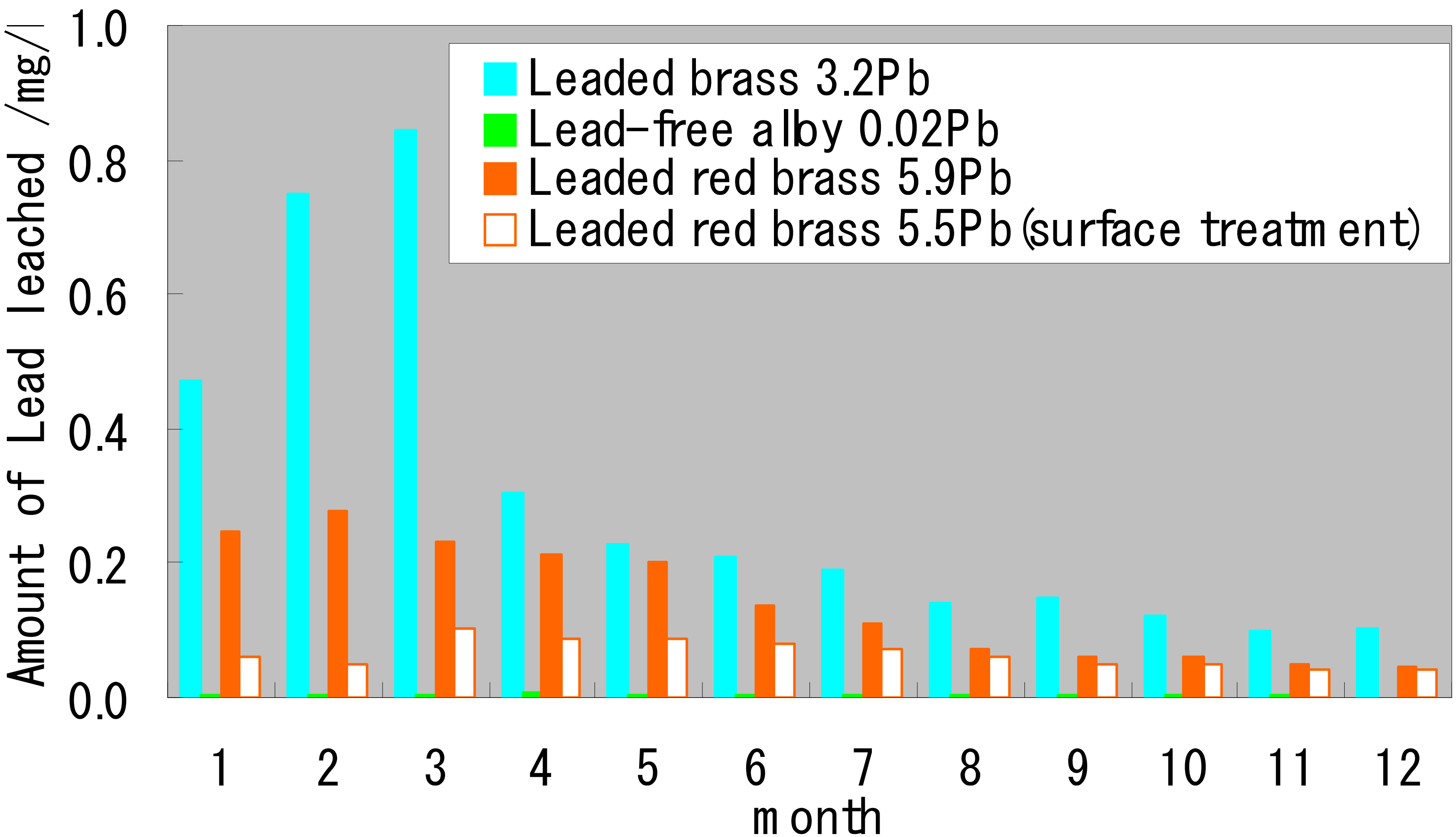
mg/L

Lead leaching characteristics into tap water



Lead leaching depends on lead content of a material
and affected by its corrosion resistance

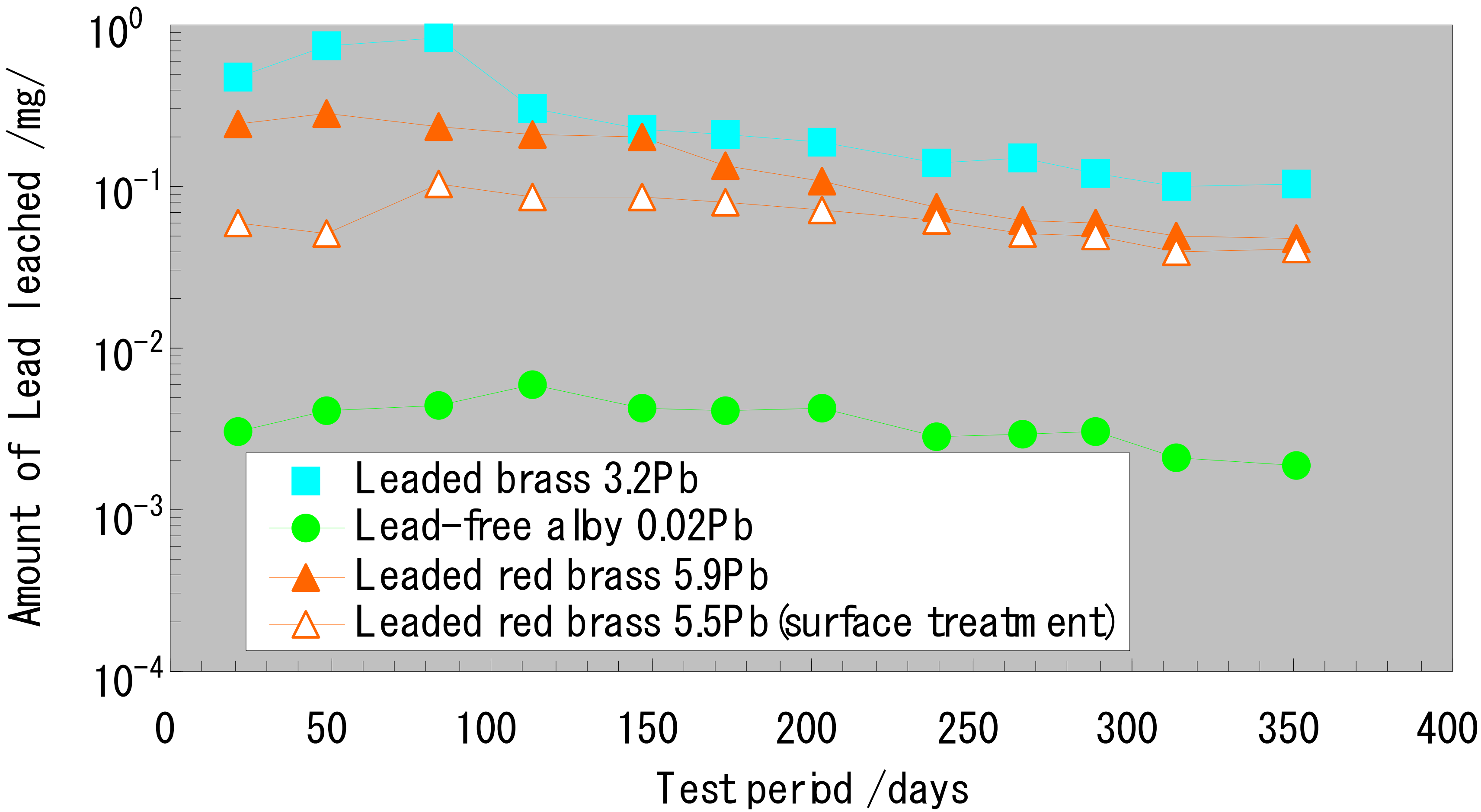
Lead leaching characteristics into CO_2 adjusted water



Lead leaching is 2 to 5 times greater in aggressive water; particularly affected by corrosion resistance

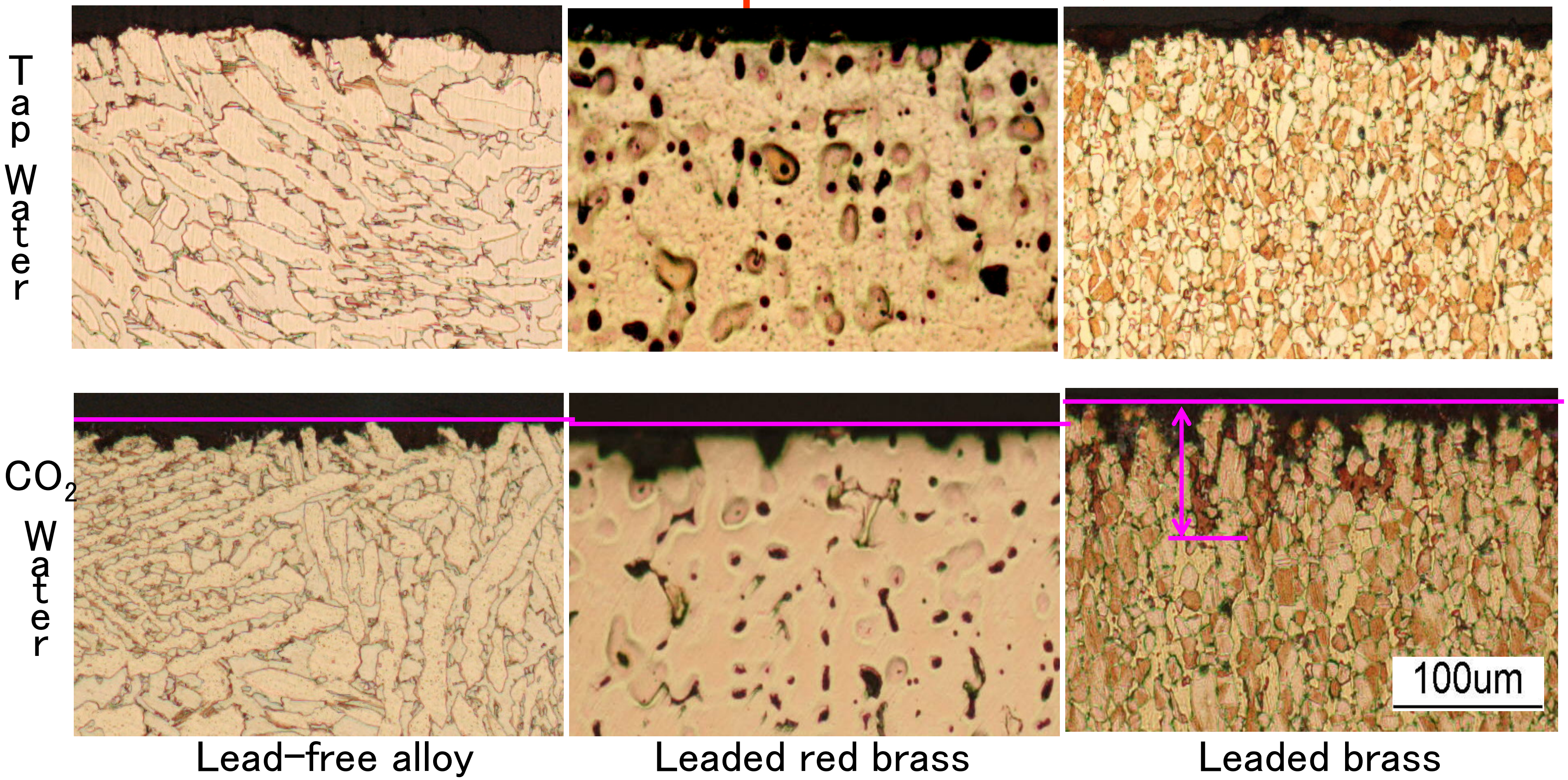
Inhibitory effect against lead leaching by surface treatment lasts for the first two months

Lead leaching characteristics into CO_2 adjusted water



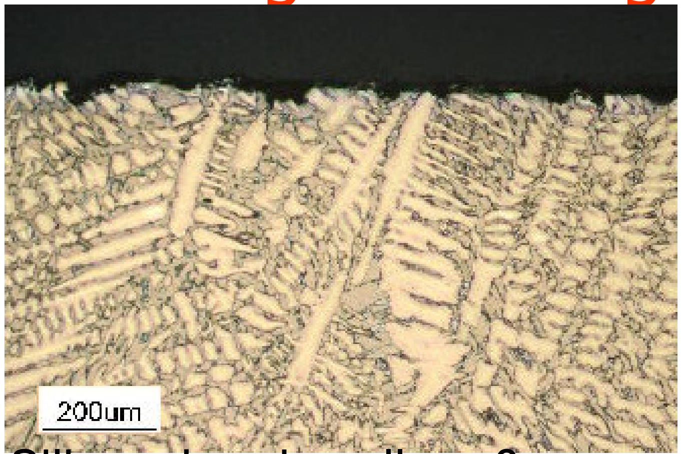
Lead leaching amount from lead-free copper alloys is two orders of magnitude less compared with leaded red brass

Microstructures of specimens (4months)

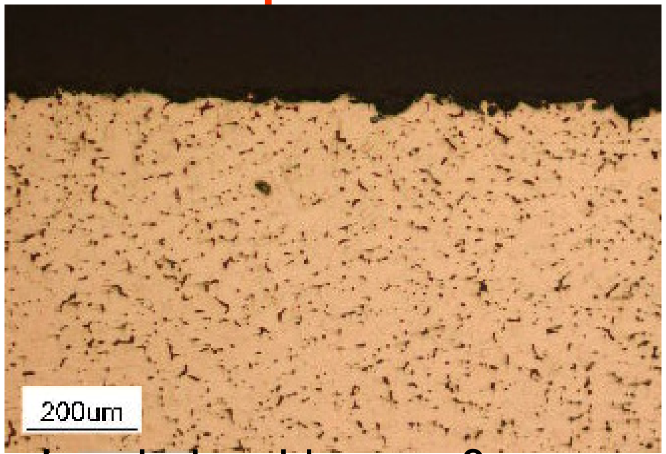


General corrosion observed for lead-free alloy/leaded red brass;
Dezincification corrosion for leaded brass

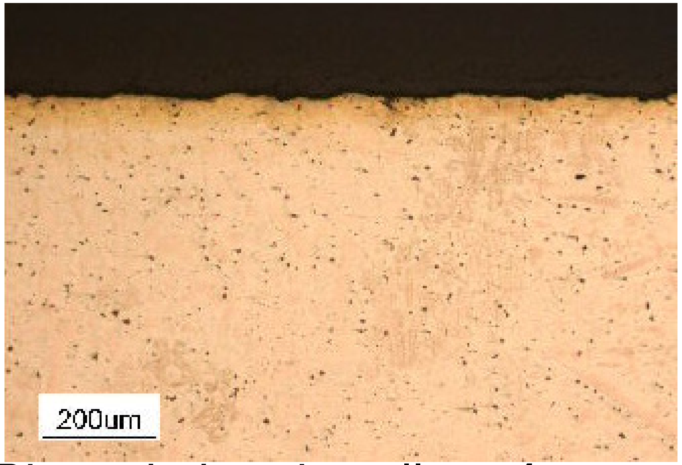
Corrosion status of various copper alloys after long-term usage in actual tap water



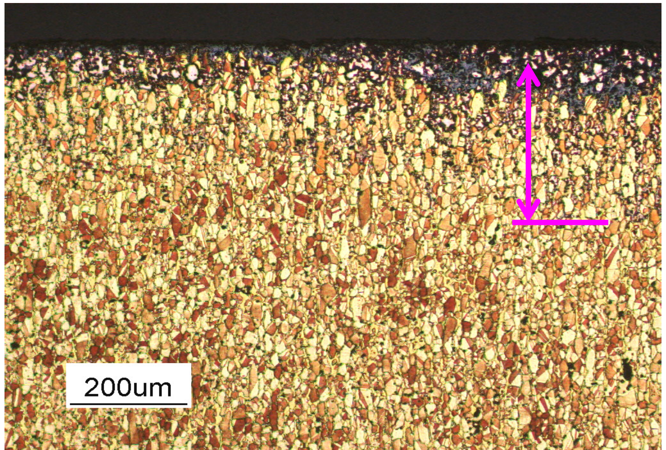
Silicon-bearing alloy 8years
(75.9Cu-2.9Si-Rem.Zn)



Leaded red brass 8years
(85.3Cu-5.9Pb-4.3Sn-Rem.Zn)



Bismuth-bearing alloy 4years
(88.1Cu-1.7Bi-4.5Sn-Rem.Zn)



Leaded brass 5years
(59.5Cu-3.1Pb-Rem.Zn)

Both silicon-bearing and bismuth-bearing copper alloys show good corrosion resistance with only a very slight amount of lead leaching

Conclusions

- ■Lead-free copper alloys started to be widely used in 2003 after the drinking water standard for lead was revised to 0.01mg/L.
- ■Lead-free copper alloys are divided broadly into two groups: bismuth-bearing copper alloys and silicon-bearing ones. Wrought copper products were standardized in industry in 2005. JIS designates castings in 2006 while wrought copper products are scheduled in 2010.
- ■Lead leaching amount depends on lead content of a material and is affected by water quality as well as corrosion resistance (dezincification corrosion resistance) of the material. Dezincification corrosion is accelerated in aggressive test water, leaching lead 2 to 5 times as much.
- ■Inhibitory effect against lead leaching by surface treatment is acknowledged for the first two months or so, although lead leaching increases due to long-term usage or water quality condition.