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Lead leachate from rubies undergone heat treatment process

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Abstract

Low quality rubies are usually undergone heat treatment to improve their color and clarity. Some chemical additives may have been added during the treatment. Consequently, some toxic elements, particular lead, have been concerned as well as durability of the treated stones. Lead leachates from treated ruby have therefore been investigated; besides, changes of color and clarity have also been observed throughout the experiment. Three-Stage Sequential Extraction Procedure (BCR) was applied for leaching experiment. This process consists of 3 steps including BCR1 (exchangeable step), BCR2 (reduction step) and BCR3 (oxidation step). This procedure has been suggested to represent natural processes that may altered materials including hazardous one. Apart from regular procedure, we also rearrange the step orders. This aims to find out the most effective condition of lead leaching. The results indicate that the most effective step seems to be BCR 3 which is an aggressive reaction compared to the other steps. However, BCR 2 also yields the highest lead concentration after activating initially by BCR I in series I. On the other hand, BCR1 is unable to extract lead from the treated ruby. Moreover, the appearances of rubies in each series have been altered towards the experimental steps and well corresponded to the concentrations of lead in leachate.

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1. Introduction

Thailand is a world famous market of colored stone. This is because of the good quality of natural gemstones sources, especially ruby and sapphire, together with the skilled craftsman for gem cutting as well as professional jewelry design and setting. Recently, good quality gem materials have reduced against increasing of price. This situation makes the lower quality gem material attracted the suppliers since their quality can be improved by heating process. According to the process heating with gas feeding, the changes in chemical structure of trace elements inside the stone may improve their color and clarity; this process is then so-called “classical heat treatment process” [Chucharuwong, 1999]. This process has been widely accepted in the international gem markets, although a few chemical additives such as borax may also be added during the heat treatment for crack healing and consequent clarity improvement. However, heat treatments have been modified for a few decades; some chemical additives may have been added in the process with trial and error by the gem treaters. These also include lead glass which may lead environmental impact, particular human health, in case they can be altered by natural process and/or daily chemical reactions.

Up to date, none of organization has paid attentions to the harmful of the chemical residue left in these treated gemstones. Normally, these chemicals are possibly leached out during human daily life such as slightly acidic conditions (pH less than 7) when exposure to lime and lemon juices (pH 2.0-2.5), beer (pH 4.5-5.0), orange juice (pH 3.0-3.5) [Nueanuansuwan, 2006] cow milk (pH 6.4-6.8) [Chuanchuen and Amonsin, 2006]. Moreover, human skins may also change slightly to acidic condition when sweat is excreted. Reducing conditions on skin can be happened by surrounding hydrogen and carbon dioxide. Utilities of toxic or corrosive chemicals in everyday life, such as calcium hypochlorite ($\text{Ca}(\text{OCl}_2)_2$) in cloth bleaching, sodium chlorate (NaClO_3) in paper bleaching, disinfectant in tap water or swimming pool as well as oxygen gas in atmosphere, may leach oxidizing condition.

In this study, Three-Stage Sequential Extraction Procedure or BCR test which has been suggested by the Standard, Measurements and Testing program (SM&T), formerly called the “Community Reference Bureau” [Rauret et al., 1999] was applied for the leaching procedure of treated rubies claimed as classical heat treatment. This method has been used to determine heavy metal concentrations, especially cadmium, chromium, copper, lead, manganese, nickel, vanadium and zinc in soil or sediment. BCR three stages **era** composed of exchangeable, reduction, and oxidation steps. Kanjanabut et al., [2010] investigated the lead contents in lead glass-treated ruby from two companies and found that the lead contents increased towards steps of testing due to more corrosion of gems. However, in natural conditions, these three steps of leaching do not continuously occur in order. Therefore, this study was planned to alternate steps of the suggested sequences and investigated the effect of leaching steps to the lead content obtained.

2. Material and Method

2.1. Sample Source

Treated rubies were collected from 7 factories, nine stones of each factories which they announce classical heat treatment.

2.2 Three-Stage Sequential Extraction Procedure (BCR)

Each treated ruby was followed the leaching procedure of three-stage sequential extraction procedure (BCR), including: 1) Exchangeable step (BCR 1), 40 ml acetic acid (0.11 mol/l^{-1}) was added, followed by 16 h shaking; 2) Reduction (BCR 2), 40 ml hydroxylamine hydrochloride (0.5 mol/l^{-1}) was added, followed by 16 h shaking and 3) Oxidation (BCR 3), 10 ml hydrogen peroxide (8.8 mol/l^{-1}) was added, followed by heating at $80 \pm 2^\circ\text{C}$ using hotplate until volume reduced to 3 ml, then 10 ml hydrogen peroxide (8.8 mol/l^{-1}) was added

and further heating at $80\pm 2^{\circ}\text{C}$ until 1 ml of solution remained, ammonium acetate (1.0 mol/l^{-1}) was finally added to adjust the volume to 50 ml followed by 16 h shaking.

2.3 Sequential Orders

Sequential orders of BCR procedures were divided into 3 series as shown in Table 1

Table 1 Experimental series of BCR step procedures

Experimental steps	Three-stage sequential extraction procedure)BCR three stages		
	series I	series II	series III
step 1	BCR 1	BCR 2	BCR 3
step 2	BCR 2	BCR 3	BCR 1
step 3	BCR 3	BCR 1	BCR 2

2.4. Lead Concentration

All solutions obtained from leaching steps were analyzed for lead concentration using Atomic Absorption Spectrometer (Perkin Elmer, Analyst 800).

2.5. Ruby Appearance

Observations of the gemmological appearance were carried out and photographed before and after all leaching steps.

3. Results and Discussion

The results of lead concentration (Tables 2-8) extracted from each series are described below.

3.1. Series I (BCR 1, BCR2 and BCR 3)

According to Series I, the highest lead concentrations leached from treated ruby seems to be extracted from BCR 2 (reduction step) except samples from factories 5 and 6 which BCR 3 gave more effect. The amounts of lead extracted from each step agreed well with the gemmological appearance which number of cracks was clearly appeared after passing BCR 2.

3.2. Series II (BCR 2, BCR3 and BCR 1)

BCR 3 (oxidation step) yielded significantly the highest lead concentration among the other steps. In addition, cracking in rubies is clearly seen in this step. However, samples from factories 1 and 7 seem to be exception.

BCR extraction appear to have no effect to treated rubies from factory 7 which lead concentration and cracking could not be observed throughout the tests.

Table 2 Lead concentrations in BCR leaching solutions (Factory 1).

Ruby No.	Pb concentration)mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	50.4	0
2	0	79.1	0
3	0	50.9	0
Avg \pm SD	0	60.1	0
	Series 2		
	BCR2	BCR3	BCR1
4	0	0	48.4
5	0	0	90.3
6	0	60.1	60.4
Avg \pm SD	0	20.0	66.4
	Series 3		
	BCR3	BCR1	BCR2
7	0	161.9	0
8	97.1	136.2	0
9	71.3	59.4	0
Avg \pm SD	56.1	119.2	0

Table 3 Lead concentrations in BCR leaching solutions (Factory 2).

Ruby No.	Pb concentration)mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	68.4	0
2	0	152.0	0
3	0	114.7	0
Avg \pm SD	0	111.7	0
	Series 2		
	BCR2	BCR3	BCR1
4	0	14.2	16.3
5	0	45.0	25.8
6	0	44.4	28.9
Avg \pm SD	0	34.5	23.7
	Series 3		
	BCR3	BCR1	BCR2
7	95.2	85.0	0
8	178.2	114.5	0
9	78.0	85.4	0
Avg \pm SD	117.1	95.0	0

Table 4 Lead concentrations in BCR leaching solutions (Factory 3) .

Ruby No.	Pb concentration)mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	26.4	20.6
2	0	17.9	13.5
3	0	33.3	23.1

Avg \pm SD	0	25.9	19.1
Series 2			
	BCR2	BCR3	BCR1
4	0	18.0	8.5
5	15.7	19.9	11.2
6	19.8	39.5	16.8
Avg \pm SD	11.8	25.8	12.2
Series 3			
	BCR3	BCR1	BCR2
7	72.4	51.7	0
8	20.3	25.8	0
9	36.6	0	0
Avg \pm SD	43.1	25.8	0

Table 5 Lead concentrations in BCR leaching solutions (Factory 4).

Ruby No.	Pb concentration (mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	21.0	10.7
2	0	27.1	14.9
3	0	36.6	21.2
Avg \pm SD	0	28.2	15.6
Series 2			
	BCR2	BCR3	BCR1
4	9.2	11.5	3.3
5	0	14.4	5.1
6	0	16.0	4.7
Avg \pm SD	3.1	14.0	4.4
Series 3			
	BCR3	BCR1	BCR2
7	16.6	4.1	0
8	77.5	12.6	0
9	49.2	9.1	0
Avg \pm SD	47.8	8.6	0

Table 6 Lead concentrations in BCR leaching solutions (Factory 5).

Ruby No.	Pb concentration (mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	21.6	25.4
2	0	33.5	37.1
3	0	27.3	29.4
Avg \pm SD	0	27.5	30.7
Series 2			
	BCR2	BCR3	BCR1
4	17.5	27.1	6.8
5	18.0	24.4	6.4
6	22.2	16.3	0
Avg \pm SD	19.2	22.6	4.4
Series 3			
	BCR3	BCR1	BCR2

7	21.0	0	0
8	35.2	0	0
9	39.1	0	0
Avg ± SD	31.8	0	0

Table 7 Lead concentrations in BCR leaching solutions (Factory 6).

Ruby No.	Pb concentration)mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	35.1	15.8
2	0	0	13.0
3	0	0	13.3
Avg ± SD	0	11.7	14.0
	Series 2		
	BCR2	BCR3	BCR1
4	65.9	46.0	0
5	18.6	20.6	0
6	27.2	30.2	0
Avg ± SD	37.2	32.3	0
	Series 3		
	BCR3	BCR1	BCR2
7	47.4	11.4	7.7
8	24.1	10.3	6.2
9	25.0	8.6	2.6
Avg ± SD	32.2	10.1	5.5

Table 8 Lead concentrations in BCR leaching solutions (Factory 7).

Ruby No.	Pb concentration)mg/kg)		
	Series 1		
	BCR1	BCR2	BCR3
1	0	71.6	54.7
2	0	76.4	0
3	0	98.4	0
Avg ± SD	0	82.1	18.2
	Series 2		
	BCR2	BCR3	BCR1
4	0	0	0
5	0	0	0
6	0	0	0
Avg ± SD	0	0	0
	Series 3		
	BCR3	BCR1	BCR2
7	0	29.8	0
8	0	43.2	0
9	0	58.3	0
Avg ± SD	0	43.8	0






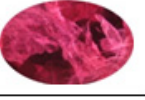
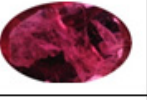



Before testing Series 1	Ruby appearance and lead concentration (mg/kg)		
	BCR1	BCR2	BCR3
			
Factory No 2	0	68.4	0
Series 2	BCR2	BCR3	BCR1
			
Factory No 2	0	45.0	25.8
Series 3	BCR3	BCR1	BCR2
			
Factory No 2	78.0	85.4	0

Fig.1 Comparison of gemological appearance of ruby and lead leached from BCR step (represented by samples of factory 2)

3.3. Series III (BCR 3, BCR1 and BCR 2)

BCR 3 (oxidation step) usually yielded the highest effect on extraction. Except samples from factories 1 and 7, BCR 1 obtained higher lead concentrations than those of BCR3. For samples of factories 2 to 6, cracks of rubies were appeared significantly by BCR3 step which they are compatible to lead concentrations in leachate. On the other hand, samples of factories 1 and 7 were clearly cracked after BCR1 test.

The extraction of lead and cracking can be representatively shown and compared by samples from factory 2 (Fig. 1).

4. Conclusions

(1) It is noticeable that ruby undergone classical heat treatment process, which were claimed to have no lead compound, may yield lead contents ranging from 0-162 mg/kg

(2) According to series I, treated rubies yield the highest lead content in BCR 2. For series II, BCR 2 has been carried out initially but it yield lower lead contents than that obtained from series I. This can suggest that BCR 2 may yield higher efficiency after activated by other BCR steps.

(3) Results from all experimental series suggest that the most effective step seems to be BCR 3.

(4) On the other hand, BCR1 has the least efficiency.

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