Copper Extraction Using Aluminum in Acidic Leachate Media

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Abstract

Copper is found in several minerals with varied elemental composition. For instance, copper minerals occur as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), cuprite oxide (Cu_2O), and malachite ($Cu_2CO_3 (OH)_2$) among many other minerals. In Kenya, extraction of valuable minerals like copper is hampered by high capital and technological investment requirements. Mineral ores found in Tharaka sub – county in Tharaka Nithi County in Kenya in particular contains significant concentrations of copper which are worth extraction. These minerals cannot be exploited due to financial and technological constraints. However, efficient and cheaper methods of extraction of copper with affordable technology are currently required. Electrolysis of copper leach solution after reaction of ground ore with acid has been done. Since the available methods involve the use of large amount of power for large scale production, alternative method for extraction has been investigated. The method involves dipping aluminum in acidic leach solution at room temperatures. The copper recovered was found to contain 80 to 90% purity depending with ore composition.

1. Introduction

Copper is one of the coinage metals which are widely used to make things like coins. It is used in making electrical wires, refrigerators, water pipes, etc. Copper occur naturally as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS), cuprite oxide (Cu_2O), and malachite ($Cu_2CO_3(OH)_2$) (Greenwood & Earnshaw 1997). A study on kinetics of copper cementation onto iron, zinc and aluminium powders at 60 ºC and pH 1 have been done. The studies have shown that three reductants (Fe, Zn, and Al) cemented copper very differently (Karavasteva 2005). Aluminium displaced copper less that either iron or zinc and also dissolved significantly less. From the study, the passivity of aluminium was due to the oxide layer on its surface. Aluminium has never been used in extraction of copper yet it is placed above copper and iron on the electrochemical series (Milazzo *et al.* 1978; Bratsch 1989; Colom *et al.* 1985).

2. Methodology

2.1 Materials and reagents

All reagents were of analytical grade and millipore water was used to make all the solutions in this study unless otherwise stated. Hydrochloric acid sulphuric acid was procured from Kobian (K) ltd. Scrap aluminium metals were bought from scrap metal dealers.

2.2 Sampling

Samples were obtained from Maragwa location in Tharaka North Sub - County in Tharaka Nithi County at locations 0º18'S38º8'E and 0º21'S38º11'E. Random sampling was used to obtain samples from ten quarries which are within one to two kilometres apart from each other. A mattock was used to dig and break the rocks while a shovel was used to scoop out the soil and rocks. A kilogram of mineral samples was collected using the same

About 250g of each rock samples was weighed and put in a paper bag and transferred to the oven for drying at 105 ºC for 9 hours. Samples were then removed from the oven and cooled. A mass of 100 g of the sample were pulverized to 250 micro millimeters using a ball mill. The samples were then used for several analyses.

2.4 Sample preparation for XRD analyses

About 30g of pulverized mineral samples was put in sample holders. The samples were then loaded on X - ray difractometer for analysis of minerals using data collector software (Mutembei *et al*. 2013).

2.5 Sample preparation for XRFS analyses

About 10g of pulverized samples was mixed with 5.0 g of analytical grade starch flux and the mixture made into pellets. The pellets were then put into XRF machine for analysis (Mutembei *et al*. 2013).

2.6 Sample preparation for AAS analyses

About 0.1g of the sample was weighed and put into 125 - ml plastic container. One millilitre of concentrated aqua-regia (1:3, Nitric acid to hydrochloric solution) was added followed by 3.0 ml of hydrofluoric acid. The sample was left to digest for at least 8 hours. 50.0 ml of saturated boric acid was added then allowed to react for one hour. The solution content was then topped up to make 100.0 ml using distilled water. Samples were then analysed alongside the standards (Mutembei *et al*. 2013).

2.7 Sample preparation for copper leach solution

About 5.0g of the sample was weighed and put into 125-ml sample bottles. 80.0ml of 1.0M of HCl was added and left to react for about 3 hours. The samples were filtered using whatman filter paper number 110 mm. The residue was washed using distilled water and the filtrate transferred into 100ml volumetric flask and made to the mark using distilled water.

2.8 Extraction of copper using aluminium

One hundred milliliters of 1.0M hydrogen ions concentrated copper leach solution was placed into 200-ml beaker. A clean aluminium rod of 0.4 cm thickness was dipped into the solution and left to reacts till all copper from the solution was displaced. The copper produced was analyzed using XRFS to determine its purity

3. Results and discussion

3.1 Mineralogical and elemental composition of the rock samples

Samples were analyzed for mineralogical analysis using XRD and the results given in figure 1 and 2 below shows some of the common minerals found in the ores.
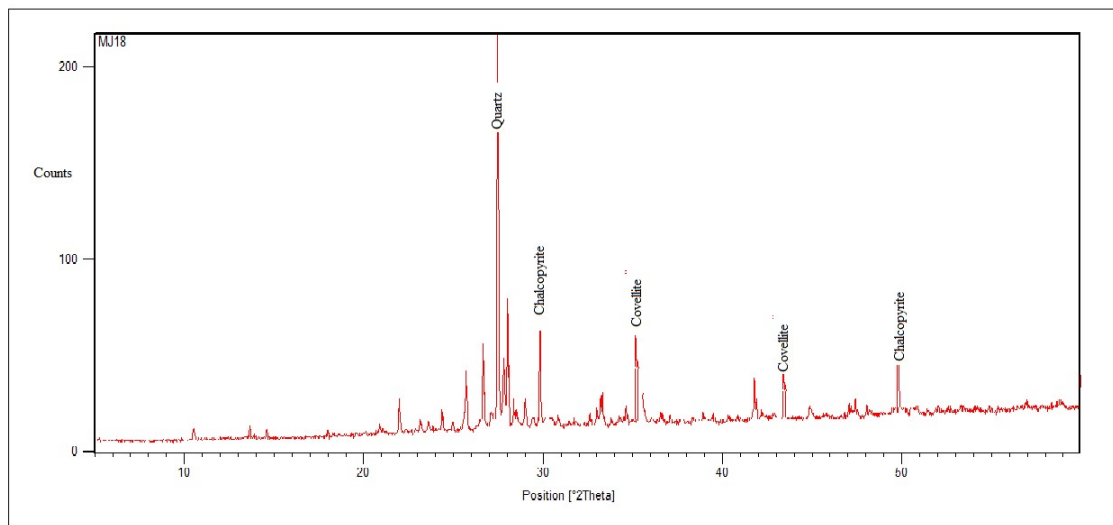

Figure 1. Common minerals in sample 3238.

Table 1. Percentage elemental composition of minerals from different deposits using AAS

|	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	CuO	MgO
Sample Reference	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE
3234	35.87± 0.08	3.59± 0.03	0.69± 0.02	12.13± 0.06	23.65± 0.08	0.63± 0.04	0.20± 0.04	13.09± 0.05	1.93± 0.02	2.41± 0.02	4.16± 0.03
3238	42.47± 0.09	10.78± 0.01	2.71± 0.04	13.08± 0.08	10.67± 0.02	1.74± 0.02	0.52± 0.33	10.07± 0.09	4.40± 0.02	5.51± 0.03	1.84± 0.02
3240	74.28± 0.12	3.23± 0.02	2.43± 0.01	9.04± 0.08	1.06± 0.02	0.46± 0.05	0.06± 0.02	1.55± 0.02	3.24± 0.06	4.05± 0.07	1.11± 0.03
3244	47.09± 0.06	14.70± 0.03	2.49± 0.01	16.37± 0.04	8.11± 0.06	0.13± 0.03	0.06± 0.02	0.04± 0.01	3.24± 0.07	4.05± 0.09	4.29± 0.04
3242	39.70± 0.09	7.68± 0.02	1.69± 0.03	5.12± 0.54	13.97± 0.04	1.04± 0.11	0.29± 0.01	20.41± 0.04	6.66± 0.03	8.33± 0.03	3.19± 0.02
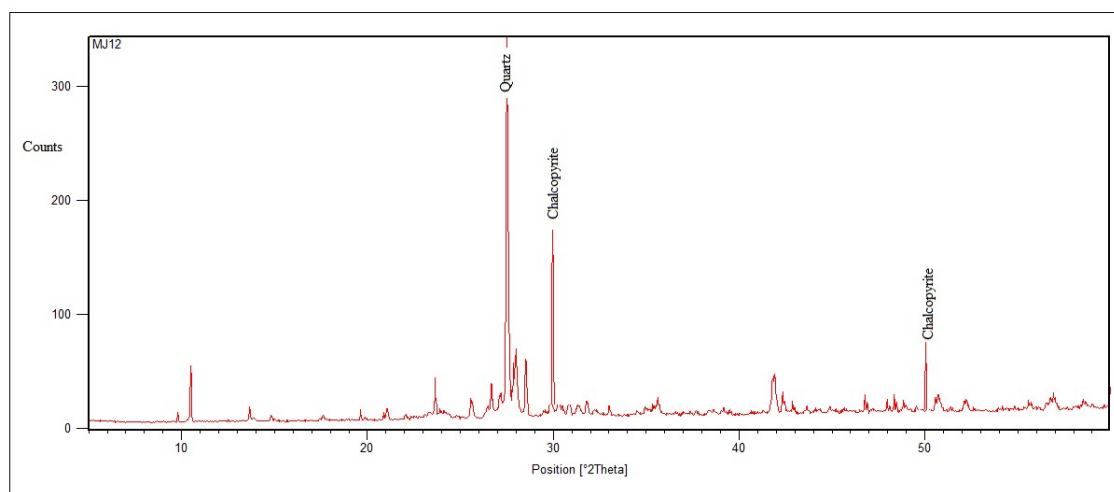
Figure 2. Common minerals in sample 3244.

Most of the deposits were found to contain chalcopyrite mineral which is shown by a peak at 2theta angle of 30° and at 50° and covellite mineral at 2theta angle of 35.5 and 43.5. Elemental analysis using AAS and XRFS was carried on the samples and the results were given in the tables 1 & 2 and statistical comparison of the methods of analysis given in table 3 below.

Table 3. Showing statistical comparison of the copper obtained using the two methods of analysis

	AAS	XRFS
Sample Reference	Mean±SE	Mean±SE
3234	1.93±0.02[a]	1.96±0.01[a]
3238	4.40±0.02[b]	4.43±0.01[b]
3240	3.24±0.06[c]	3.19±0.02[c]
3244	3.24±0.07[d]	3.19±0.01[d]
3242	6.66±0.03[e]	6.69±0.01[e]
P-value	<0.001	<0.001

From the results, mean values followed by the same small letter within the same row are not significantly different ($\alpha=0.05$, sktest). Therefore, there is no significance difference in the results obtained using the two methods. This shows that copper ores in Tharaka Nithi County have good mineralogical composition of 1 to 7%. This composition is the best than the one mined in Uganda (0.48 - 2 % Cu) (Zambian Mining Magazine 2013), South Africa (0.56 - 0.7% Cu) (Groves & Vielreicher 2001), Botswana (1.3 and 1.5%) (Discovery Metals Ltd 2012), and in Zambia (0.5 to 2.3% copper) (First Quantum Minerals Ltd 2013). Therefore these minerals are viable for extraction for economic gain.

Table 2. Percentage elemental composition of minerals from different deposits using XRF

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	CuO	MgO
Sample Reference	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE	Mean± SE
3234	35.85± 0.06	3.56± 0.05	0.69± 0.02	12.11± 0.05	23.67± 0.06	0.66± 0.07	0.27± 0.07	13.10± 0.02	1.96± 0.01	2.45± 0.02	4.12± 0.08
3238	42.48± 0.04	10.76± 0.04	2.67± 0.03	13.05± 0.07	10.61± 0.03	1.70± 0.03	0.33± 0.03	10.06± 0.10	4.43± 0.01	5.54± 0.01	1.98± 0.04
3240	74.28± 0.09	3.33± 0.05	2.45± 0.05	9.03± 0.08	1.08± 0.01	0.39± 0.02	0.03± 0.05	1.56± 0.03	3.19 0.02	3.99± 0.02	1.03± 0.02
3244	47.04± 0.06	14.73± 0.05	2.46± 0.04	16.37± 0.04	8.10± 0.04	0.18± 0.09	0.09± 0.03	0.04± 0.01	3.19± 0.01	3.98± 0.01	4.23± 0.09
3242	39.73± 0.04	7.65± 0.10	1.70± 0.01	5.24± 0.06	12.91± 0.02	1.06± 0.07	0.28± 0.02	20.26± 0.09	6.69± 0.01	8.36± 0.09	3.22± 0.02

3.2 Optimisation of time taken for reduction of all copper from ore at different concentration using aluminium rod

About 100 ml of the prepared leach solution was put into six beakers of 250-ml volume. Varied volumes of concentrated hydrochloric was added to make concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5 M. Time taken for the aluminium scrap metal to displace all copper at different concentration is given in figure 3 below.
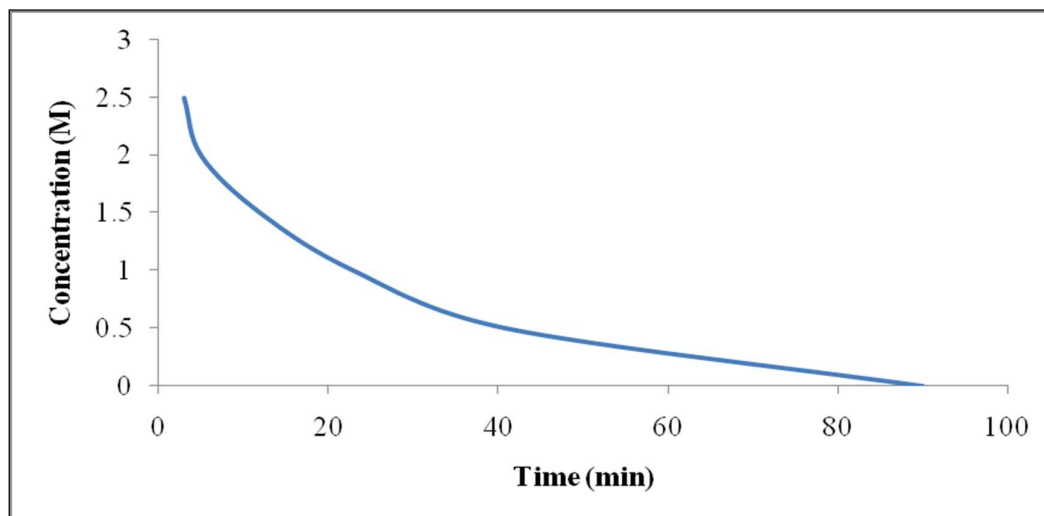
Figure 3. Time taken for complete copper reduction against concentration of the leach solution

The results from the experiment show that the time taken for the reduction of copper from the leach solution increased with decrease in the concentration of the leach solution. The concentrations of about 2.0M were appropriate for effective extraction of copper for about 5 minutes. At concentration above 2.5M HCl, all copper gets reduced within less than 3 minutes and later the copper produced reaches equilibrium with solution. This makes copper to form fine precipitate which are difficult to filter. In addition, concentrations of above 2.5M leads to oxidation of copper produced to CuO. This occurs because the reaction of aluminium with acid is an exothermic reaction. For mass copper extraction, 2M HCl is appropriate which will take about 5 minutes for reduction. To reduce time taken for complete reduction at the same reaction rate, several aluminium rods can be used. However, in all cases constant mass of copper produced was almost the same. The copper produced was having 82 to 89% purity. The relationship between copper produced with rate of reaction was also investigated. The rate of copper reduction was found to increase with the concentration of the leach solutions as shown in figure 4 below.
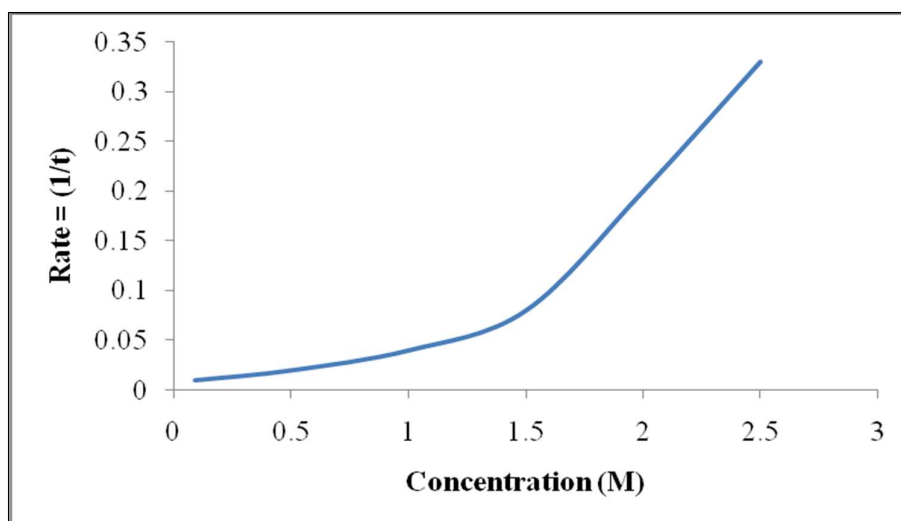

Figure 4. Concentration of leach solution against the rate of the copper reduction

After optimization, aluminium half-cell was used to extract copper from several deposits at both level A and B and results given in tables 6 and 7, and figure 5 and statistical mean of extract given in table 8 below.

Table 6. Copper extract at level A using aluminium half-cell reaction

Sample no.		Trial 1(gms)	Trial 2 (gms)	Trial 3 (gms)	Average(gms)	% Extract A	% copper purity
3227	C	0.437	0.45	0.442	0.443±0.007	8.8	88.2
3230	F	1.623	1.65	1.596	1.623±0.027	32.4	86.9
3231	G	1.163	1.212	1.274	1.216±0.056	24.4	85.8
3232	H	1.017	1.057	0.979	1.017±0.039	20.4	85.1
3233	I	0.368	0.381	0.352	0.367±0.015	7.4	85.5
3234	J	0.341	0.356	0.363	0.353±0.011	7	84.9
3238	N	1.031	0.98	0.975	0.995±0.031	20	87.2
3240	P	0.863	0.871	0.868	0.867±0.004	17.4	84.6
3244	Z	0.733	0.739	0.744	0.738±0.006	14.8	85.1
3242	W	0.347	0.363	0.355	0.355±0.008	7.2	87.9

Table 7. Copper extract at level B using aluminium half-cell reaction

| Sample no.		Trial 1(gms)	Trial 2 (gms)	Trial 3 (gms)	Average(gms)	% Extract B	% copper purity
3227	C	0.428	0.386	0.386	0.4±0.024	8	83.7
3230	F	1.273	1.223	1.092	1.196±0.093	24	86.3
3231	G	1.693	1.652	1.649	1.665±0.025	33.4	88.2
3232	H	0.838	0.831	0.795	0.821±0.023	16.4	82.7
3233	I	0.688	0.621	0.587	0.632±0.051	12.6	85.9
3234	J	0.371	0.348	0.395	0.371±0.024	7.4	84.4
3238	N	1.363	1.371	1.283	1.339±0.049	26.8	88.6
3240	P	0.867	0.829	0.836	0.844±0.02	16.8	86.3
3244	Z	0.946	0.846	0.893	0.895±0.05	17.8	81.8
3242	W	0.452	0.407	0.396	0.418±0.03	8.2	87.4
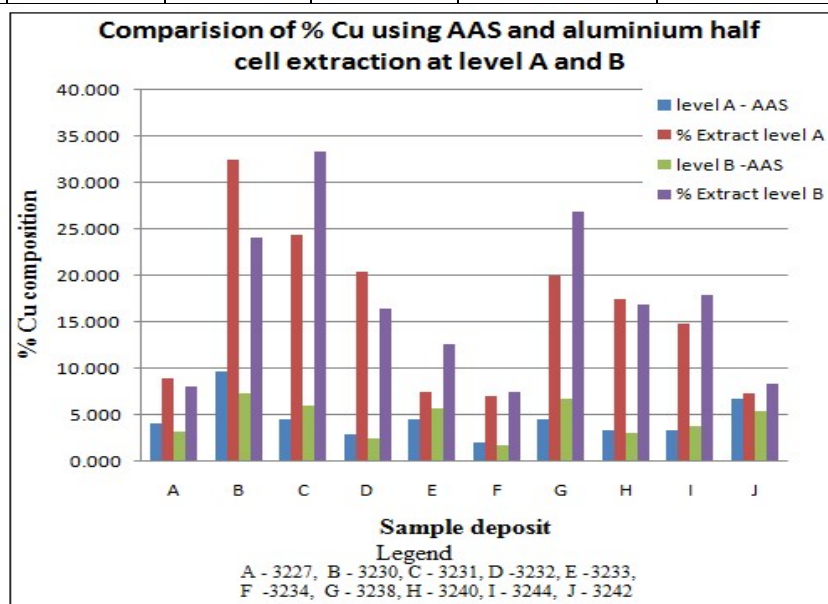
Figure 5. Comparison of percentage Cu before and after extract using aluminium at level A and B.

Table 8. Mean copper extract for both level A and B using aluminium half-cell reaction

	Mean±SE	p-value
% Extract level A	15.98±8.57	0.6312
% Extract level B	17.14±8.72	0.5999

P-value is greater than 0.05. The amount of copper extract using aluminium at level A and B is significantly different. (α=0.05, sktest)

From the results the purity of copper extract increased significantly in all the samples. Al metal is very reactive and placed above hydrogen and copper on the reactivity series. In neutral leach solution, aluminium is less reactive due to the formation of stable aluminium oxide layer. After acidification using hydrochloric acid, the oxide reacts with hydrogen ions forming water as shown in equation 1.

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \qquad (1)$$
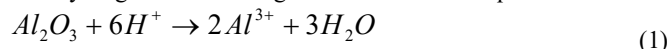
After the removal of the oxide layer, the rate of oxidation of the aluminium proceeds proportionally with the concentration of hydrogen ions in the leach solution. A mole of aluminium gets oxidised and at the same time reduces two moles of hydrogen ions to one mole of hydrogen gas as given in equations 2 and 3 below.

$$Al \rightarrow Al^{3+} + 3e^- \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

From the equations 2 and 3 above, one mole of electrons accumulates on the aluminium electrode for every mole of aluminium oxidized. This causes the build-up of electrons on the aluminium metal. The whole reaction becomes the aluminium half-cell reaction. The build-up of electrons later causes reduction of the copper ions to metal around the electrode. The experimental setup is shown in figure 6. The copper produced was washed with distilled water and then dried at temperatures between 25 to 40ºC.
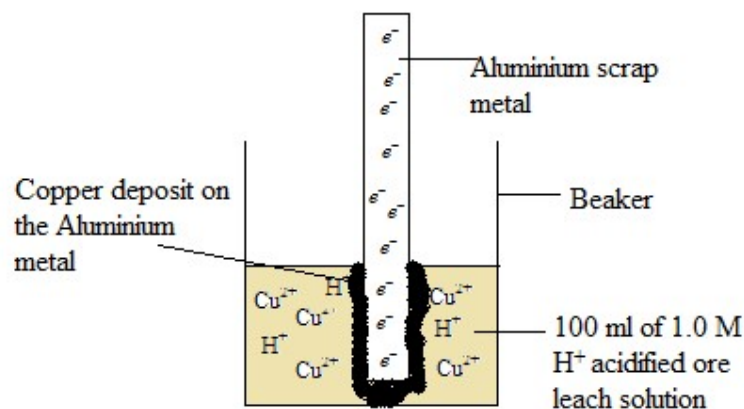

Figure 6. A diagram of copper reduction using aluminium half cell reaction

4. Conclusion

This method of copper displacement from the leach solution has proven to be successful ways of extraction of copper from ore. The copper produced contains 80 to 90% purity. The method can be setup in any location since electricity is not a requirement.

Conflict of interest
The authors declare that there is no conflict of interest.

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