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Controlled Release Formulation of Loaded Clay with Copper Sulphate for Eradication of Schistosomiasis Snails (Bilhariasis)

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ABSTRACT. Two controlled release formulations (CRF) of copper sulphate as a molluscicide loaded onto natural clay are described. A binding agent such as cement is preferable to heat treatment. The accumulative release of copper ions in water for 6-8 weeks revealed that these CRF follow a zero order release system of theoretical life of 270-350 days. The released dose is 0.3 to 0.15 μg/ml daily which is above the lethal dose for the host schistosomiasis snails.

Different methods are used to overcome schistosomiasis. One of the methods is eradication of intermediate snail-hosts by the use of different molluscicides. It is well recognised that copper sulphate when used as molluscicide in the conventional manner suffers a number of drawbacks. Relatively large quantities must be utilised in order to avoid the rapid detoxification by suspended materials, organic life, naturally occurring negative ions, and organic complexing by various life forms (Amin 1972, Ritchie and Malek 1969).

The controlled slow release of molluscicides is the topic of this work. This concept applies to certain formulations that slowly and continuously release the toxic element in the environmental interface over a long period of time. This technique was successfully applied since 1964 in antifouling paints (Cardarelli and Caprette 1963).

In 1971, an effort was initiated to develop a controlled release copper sulphate-elastomer compound that would provide 6 or more months of copper ion release at adequate levels of snail control. Preliminary studies indicated that styrenebutadiene copolymers or natural rubber would bind and slowly release copper sulphate upon exposure to water. Different commercial products, as such

Incramide[tm], E-51 (International Copper Research Association N.Y.) in different forms have been tested and evaluated (Cardarelli and Lancaster 1971). It was demonstrated that a copper ion release between 0.065 ppm/day and 0.13 ppm/day will destroy the strain of *B. glabrata* over 30-90 days period with no gross effect on most aquatic weeds or on the sentinel fish used (*Lebistes reticulatus*) (Cardarelli 1977).

Copper toxicity in man is rare, levels necessary for chronic poisoning have been estimated at 10 times the amount common to the human diet of 2.5-5 mg uptake per day.

Since the elastomers used in the industrial preparations are made of expensive materials and need specialised techniques for their preparation, we thought it would be beneficial to formulate materials which are simpler, cheaper and yet as effective as the known industrial methods.

This was achieved by loading the toxic cations onto local natural clays, binding them in a fixed matrix, pelletising the mixture, and studying their slow release in aqueous media. This study comprised two parts. First, it was necessary to study and review the adsorption behaviour of copper ions on natural common clays mainly the kaolinite and the montmorillonite types. Second, a kinetic laboratory study of the daily release of copper ions in tap water was carried out. The kinetic order was estimated and the theoretical expected life of the loaded pellets was calculated.

Experimental

A. Adsorption Studies

The adsorption study of copper ions with different natural clays is carried as follows. 200 ml of a 10^{-3} molar copper sulphate solution are stirred with 2 g of clay. Adsorption is followed by determining spectrophotometrically the amount of copper ions taken by the clay using the diethyldithiocarbamate method (Foster dee Snell 1978). In this method, Beer's law is followed from 0.1 to 9 μg copper/ml. A standard curve is plotted between copper ion concentration versus optical density at 436 nm using a 5270 Beckman spectrophotometer. Uptake of copper ions by clay was also studied at different pHs. Two from different studied clays gave promising results. A C-4 clay found in great amounts in the Riyadh area gave a 70% uptake. It is mainly a kaolinite clay rich in Ca and Mg, and the other is C-8 phosphate clay found near the red sea area in Egypt it gave a 30% P_2O_5 content mainly a montomorillonite clay rich in Al and SiO_2 with a 65% adsorption of copper.

B. Preparation of the Controlled Release Formulations

The chosen clay either C-4 or C-8 was ground to fine mesh and sieved. Similarly solid copper sulphate pentahydrate was ground and sieved. The two ingredients were finely mixed and the binding agent was added, the paste with tap water is hand extruded through stainless steel discs of different hole diameter. The extruded pellets were cut to 3-5 mm lengths and left to dry for 48 hr and used as such in the release study. Two methods were applied for binding the clay with copper sulphate. One by using white cement in the ratio 3-10% and the other using heat treatment from 350-600°C (Umesh 1970), without any cement, as shown in Fig. 1.

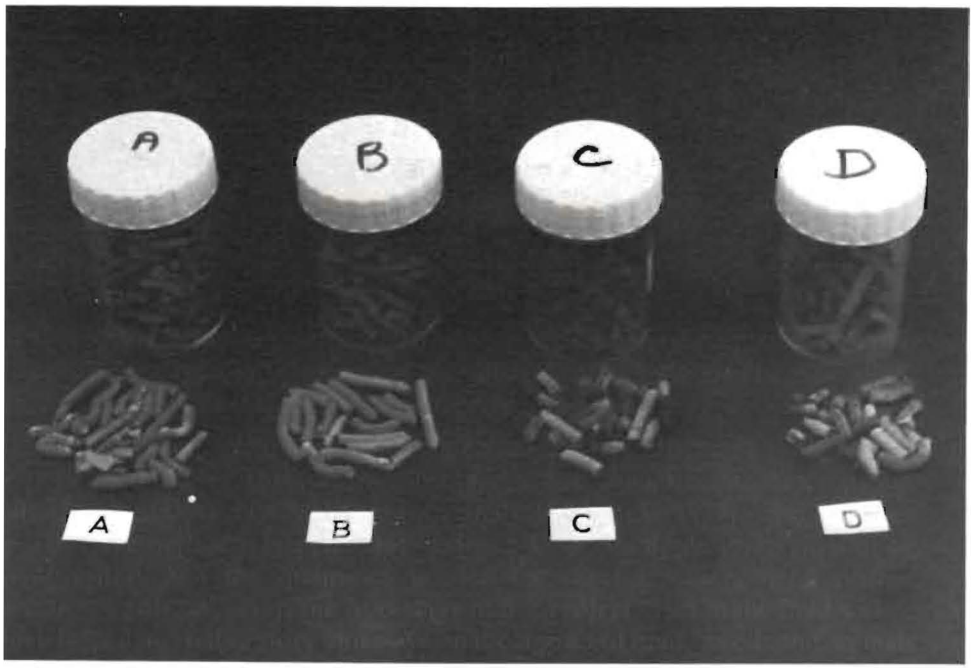

Fig. 1. Photograph of the different clay preparations.

C. Release Study

Five grammes of the dried pellets were put in a perlon bag and hanged in a beaker containing 500 ml of tap water stirred magnetically. Leaching for 2 hr was carried out first and loose copper was evaluated. The water was replaced with a fresh one for each bag and every 24 hr copper was estimated. This was repeated daily while changing the water in order not to upset the normal release of copper by the accumulated dose. This was continued for nearly 5-6 weeks (Table 1).

Table 1. Release pattern of our CRF with their theoretical life.

Clay	$C_8^{**}+50\%CuSO_4$		$C_4^{*}+50\%CuSO_4$		$C_8+20\%CuSO_4$		$C_4+20\%CuSO_4$	
treatment / time	Cement	heat	Cement	heat	Cement	heat	Cement	heat
2 hours leaching	518 mg	819	586	780	200	265	189	205
1*st* week	2.73 mg	3.08	2.45	3.68	0.91	0.70	0.63	0.56
2*nd* week	1.36 mg	2.17	1.42	2.30	0.42	0.35	0.35	0.42
3*rd* week	1.54	1.33	1.18	1.94	0.28	0.35	0.35	0.35
4*th* week	1.33	0.91	1.29	1.04	0.21	0.21	0.28	0.21
5*th* week	1.48	0.56	1.12	0.85	0.14	0.27	0.28	0.18
Calculated Theoretical life (days)	354	267	374	273				

* C_4 : a kaolinite clay rich in Ca & Mg carbonate (from Riyadh area).
** C_8 : a montmorillonite clay rich in Al & SiO_2, containing 30% P_2O_5 (phosphate clay found in Egypt).

Results and Discussion

Copper (II) taken up by the clay is of two types. One part is labile and released quickly to water usually within 10 min, the other part is more tenaciously held and is presumably ion exchanged onto the clay. A significant effect was observed on the exchange adsorption of the copper II ions by clay for different anions. The order of preference for adsorption into the clay was as a function of anion (Carter 1975).

$$SO_4^{--} > Cl^- > NO_3^- > ClO_4^-$$

Sulphate with two negative charges may have a good affinity for the positive edge of the clay crystal and this could enhance adsorption. Thus, SO_4^{--} has the correct stereochemistry to interact with the crystal edge. Copper (II) may now have an enhanced affinity for the edges (Mirzai and McWhinnie 1982).

Our choice of $CuSO_4$ for loading the clay is in accordance with the above results, *i.e.* SO_4 anion is best suited for higher adsorption and exchange. Work at pH 5-6 gives the highest yield of uptake which is fortunately the pH of tap water where copper ion solubility is not affected by carbonate-bicarbonate presence.

We loaded our clays with 50% and 20% copper sulphate pentahydrate. We bound the clays either by cement or by heat treatment.

Limits of Binding Agents

Lower ratio of 3% cement made the pellets frittable in water with total release of copper ions. Higher ratio over 5% cement did not release any copper ions. Similarly, at temperature less than 400°C, the heated pellets are swollen in water and release quickly their copper content. At above 550°C, the surface of the pellets turns partially black due to CuO formation and copper ions are difficulty released onto water.

Leaching tests of C-8 and C-4 loaded with 50% $CuSO_4$ proved that cement binding is preferable than heat binding. 20% of copper ions are released from cement binding while 33% from heat binding. This amount of copper released by leaching is loosely bound or adsorbed at the surface of the clay, while the 80% remaining nearly 2 g are firmly bound and are released slowly at the rate of 0.3.15 μg/day within the lethal dose for schistosomiasis in host snails. Kinetic study of the above formulations is carried (Fig. 2). By plotting the accumulative dose of bioactive material against time a straight line is obtained as in Fig. 3, for a pseudo zero order release system, as a result of the minute change in concentration over a short period of time. Thus, the first order rate equation, $-\,dn/dt = kn$, appeared to be zero order for small Δn. The theoretical life of a CRF is the life expectancy of the formulation under ideal conditions and is based on the assumption that the bioactive material will migrate into the solvent by the same mechanism over its entire life. The real life of a CRF can only be determined by repeated bioassay in the field and may be significantly different than the theoretical life.

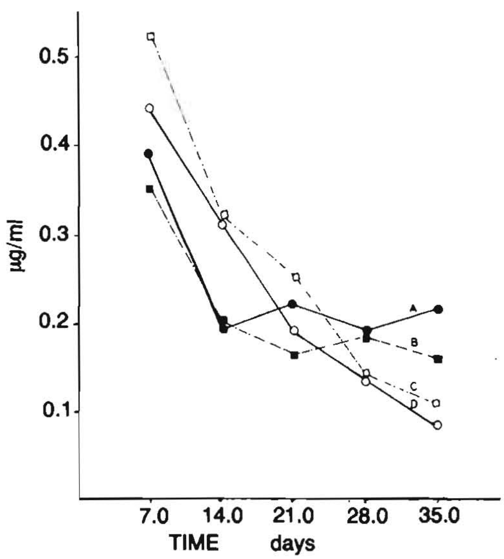

Fig. 2. Concentration of copper ions released versus time.

A- C-8 (50%-$CuSO_4$), Cement
B- C-4 (50%-$CuSO_4$), Cement
C- C-4 (50%-$CuSO_4$), Heat
D- C-8 (50%-$CuSO_4$), Heat

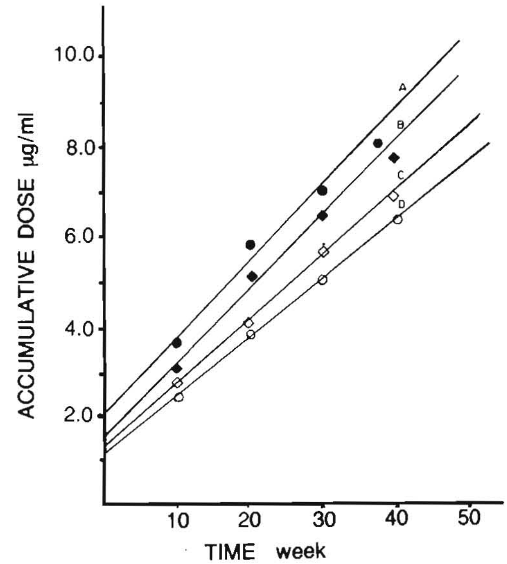

Fig. 3. Accumalative dose of copper ions released versus time.

● C-4 Heat
■ C-8 Heat
□ C-8 Cement
○ C-4 Cement
($50\% CuSO_4$)

Theoretical life for our prepared CRF can be determined either from the slope of the lines as in Fig. 3 or by empirical formulae (Sherman 1982). Theoretical life are given in the table for our different prepared CRF.

It has been observed that while organic materials tend to bind copper ions in solution or suspensions. Thus, slowing insolubilization, the inorganic materials will dissolubilize it and likely to destroy its toxicity (Cardarelli 1977). The effect of some other factors such as pH, temp. on our CRF, its applicability to still or stagnant waters and the quantities needed for flowing waters need further investigation. This, in fact, is the next stage of our project. Test in the field will be run on a later date. Laboratory bioassays on the impact of mud, weeds and animals biota on our CRF products will be carried out to estimate their real life expenctancy.

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القضاء على قواقع البلهارسيا بالتحكم البطيء لإفراز النحاس المحمل علـى الطمي الطبيعي

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في هذا البحث نشرح طريقتين لتحضير مـركبات من الـطمي المحلي المحمل بـ ٥٠٪ من كبريتات النحاس المعالجة بواسـطة الأسمنت الأبيض أو الحـرارة. وقد ثبت لنـا أفضلية استعـال الأسمنت حيث المدة الأطول لعملية الإفراز. وبـدراسة نـظام كمية النحاس المفرزة لمدة خمسة إلى ستة أسابيع وجد أنه تتبـع قانون التفاعل من الـدرجة الصفـر بعمر تقـريبي يتراوح بـين ٢٧٠ إلى ٣٥٠ يوماً. كميـة الجرعـة المقررة يـومياً تـتراوح بين ١٥ إلى ٠,٣ مايكروجرام لكل مللتر. وهذه الكمية تزيد عن الجرعة المسببة للقضاء على قواقع البلهارسيا نهائياً.