Sustainable Management of Water Resources in the Rift Valley (MAWARI) Project

Origin, Genesis and Distribution of Fluoride in the Ethiopian Rift and Development of Defluoridation Technologies

Progress Report 2: February – July, 2006

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Fluoride project is a model research project being developed to deal with the problems related to high fluoride concentrations in the Main Ethiopian Rift, which is the number one water quality and hence management problem in this part of the Rift. The project currently undertakes research activities essentially related to:

A) Source, genesis and distribution investigation;

B) Adsorption investigation using aluminium hydroxide;

C) Adsorption investigation using clays; and

D) Adsorption investigation using iron oxide coated sand.

This progress report highlights the activities performed in the last six months and stipulates our plan of action for the next six months. The structure of the report follows the instruction set by the facilitators and encompasses:

1. Specific objectives set / expected results of the period;
2. Summary of filed activity; laboratory activities;
3. Training activities;
4. Scheduled activities for the next six months; and
5. Purchases related.

1. Specific objectives set / expected results of the period

A) Source, genesis and distribution investigation

Due to the delay in the international literature survey, the initial plan of action stated in the proposal has been shifted. Hence **the specific objectives of this period were**:

- Undertaking the international literature survey on fluoride source, genesis and distribution;
- Continuing data gathering, compilation and entry from various sources; and
- Continuing map digitization.

B) Adsorption investigation using aluminium hydroxide

The specific objectives are:

- To investigate the removal of fluoride from aqueous solutions in continuous process at different operating conditions (bed depth, flow rate and influent concentration) using aluminium hydroxide as an adsorbent;
- To investigate the applicability of simple models such as Bed Depth Service Time (BDST) Empty Bed Retention Time (EBRT) and Thomas models for the design of adsorption system for fluoride by aluminium hydroxide;
- To evaluate the possibility of regeneration and reuse of the media; and
- To investigate the effect of co-existing ions on the defluoridation capacity of treated and untreated aluminium hydroxide in batch mode.

C) Adsorption investigation using clays

The specific objectives are:

- Conduct further literature review;
- Collection of different clay types from different regions of the country;
- Investigation of the adsorption capacity of the different raw clay types at different operating conditions; and
- Investigation of the adsorption capacity of treated clay at different operating conditions.

D) Adsorption investigation using iron oxide coated sand

The specific objectives are:

1. Collect and identify samples of Iron Oxide Coated Sand (IOCS) which is the by-product of iron removal ground water treatment plants;
2. Fluoride adsorption capacity of the IOCS will be tested separately in batch experiments;
3. Adsorption isotherms and kinetics will established;
4. Study the pH adsorption edge of fluoride-adsorption onto IOCS;
5. Other factors that influence the adsorption capacity will be investigated using fluoride containing distilled water as well as real water samples; and
6. Formulate recommendation for the next phase.

2. Summary of filed activities; laboratory activities; and office works

Two general activities have been performed related to fluoride project in the last six months. These are, participation and presentation of the status of the project in a MAWARI project meeting organised by facilitators in France; and fluoride project team meeting. Therefore, they are briefly reported here since they are common to the project.

MAWARI project meeting (Orleans, France)

A MAWARI project meeting organised by facilitators was held in Orleans, France on May 26 and 27, 2006. The participants include the scientific committee and facilitators of the MAWARI project and project team leaders. Dr. Dereje Ayalew, the Ethiopian scientific representative of the MAWARI project; Dr. Berhanu Gizaw, fluoride project team leader; and Dr. Tamiru Alemayehu representing the hydrogeological project of MAWARI participated from Ethiopia.

The fluoride project team leader presented the status the project. The meeting was found to be useful in assessing the performances of ours as well as other projects from Djibouti and Kenya. The outcomes of the report were communicated to the project researchers at the fluoride project team meeting held afterwards at Debere Zeit, Ethiopia.

Fluoride Project Team Meeting (Debere Zeit, Ethiopia)

The team leader of the project proposed a fluoride project team meeting after consulting other project researchers and participants of the Orleans meeting in order to brief the outcome of the meeting; assess the performance; initiate active participation; and discuss the way forward. The idea was

approved by the facilitator and as a result it was held on Thursday July 06, 2006 at Debere Zeit. A minute of the meeting has already been forwarded. The main issues and outcomes of the meeting:

- The participants were briefed on the outcomes of the meeting at Orleans, France;
- Disclosed their concern on the current information dissemination policy of the project;
- The timetable of participants disclosed;
- Underlined the need of having two PhD students; and
- Promised to work on the project actively.

A) Source, genesis and distribution investigation

Summary of office works:

Filed and laboratory activities were not scheduled for the current reporting period for the origin part of the project.

- **The international literature survey has been delayed due to various reasons but eventually has done in this reporting period.**

  The survey was done during the 2nd half of May, 2006 both at the University of Avignon and French geological Survey (BRGM). It was realised that the fluoride problem is a problem of many countries worldwide. As a result, numerous studies have been made and published. The survey was of profound importance for the project despite its tight schedule and hence on behalf of the project, the team leader would like to acknowledge the facilitators, Dr. Michel Laval and Mrs. Sylvie Orlyk of CIFEG; and the BRGM; and Prof. Yves Travi of the University of Avignon for organising the program, advising, making a conducive environment and overall hospitality they have offered.
- **Most of the collected articles on international scale have been reviewed**
- **Much of the data gathering, compilation and entry from various sources is completed**
- **Much of the map digitization has been made**
- **Local purchase of some required materials has been made**

B) Adsorption investigation using aluminium hydroxide

Summary of laboratory activities and obtained results

Batch adsorption kinetics and thermodynamic study results using aluminium hydroxide produced in our laboratory was reported in our former study (Beneberu et al., 2006[1]). In the present work, the removal of fluoride using aluminium hydroxide was studied in a fixed bed column system at different flow rate and column height. The Bed Depth Service Time design model, Empty Bed Residence Time and Thomas model were used to analyze the performance of the column and the effect of the different operating variables such as bed depth; flow rate and initial concentration were tested on these simplified fixed bed design models. Desorption experiments were conducted to evaluate the possibilities of regeneration and reuse of the media. The effects of co-existing ions on the adsorption capacity of aluminium hydroxide were also investigated in batch mode.

[1] Beneberu Shimelis, Feleke Zewge and Bhagwan Singh Chandravanshi (2006) Removal of Excess Fluoride from Water by Aluminum Hydroxide. Bull. Chem. Soc. Ethiop., 20(1), 17-34.

The breakthrough curves for the adsorption of fluoride on to aluminium hydroxide confirmed that the breakthrough volume and breakthrough time were decreased with increasing flow rate and initial fluoride concentration or decreasing bed depth. The data estimated from bed depth service time model showed that the adsorption capacity (N_o) of the adsorbent were found to be 24.07, 25.79 and 12.7 mg g^{-1} for 12, 23 and 40 mL min^{-1} flow rate, respectively. The operating line seems flatten and no significant reduction in adsorbent exhaustion rate is gained with contact time greater than about 3, 6 and 7 min for 40, 23 and 12 mL min^{-1} flow rates respectively, with the corresponding usage rate of 2.2, 0.9 and 1.3 g L^{-1}. The optimum dose for batch system in our former study was 1.6 g L^{-1} and it is close to the adsorbent exhaustion rate of 12 mL min^{-1}. The application of Thomas model has showed that the adsorption capacity is strongly dependent on the flow rate, initial fluoride concentration, and bed depth and is greater under conditions of a lower concentration of fluoride, lower flow rate and higher bed depth. And the Thomas rate constant decreases with increasing bed depth, decreasing initial concentration, and flow rate. Results concerning the effects of anions on the adsorption of fluoride on to the aluminium hydroxide showed that Cl^- and

SO_4^{2-} have very little effect on the fluoride removal capacity of adsorbent but HCO_3^- and PO_4^{3-} had a profound effect on the removal capacity of the adsorbent.

Hence it is concluded that using granular aluminium hydroxide, as an adsorbent for fluoride removal in a fixed-bed adsorption process is feasible.

C) Adsorption investigation using clays

Summary laboratory activities

Batch adsorption experiments were carried out using four different clay samples collected from Harari, Mughur and Sidamo regions. The raw clay was investigated at room temperature. Heat treatments of the four samples were conducted at various temperatures (100-700^{O}C) and the adsorption capacity were investigated. In addition the effect of particle size was studied for 5 ranges: <250 µm, 250-500 µm, 500-1000 µm 1000-1250 µm and >1250 µm. The result will be presented after the final submission of the MSc. thesis work (next reporting period).

D) Adsorption investigation using iron oxide coated sand

The following activities have been accomplished so far related to iron oxide coated sand (IOCS).

- **Bibliography for Defloridation (particularly Using Iron Oxide Coated Sand) were assessed at national level:**

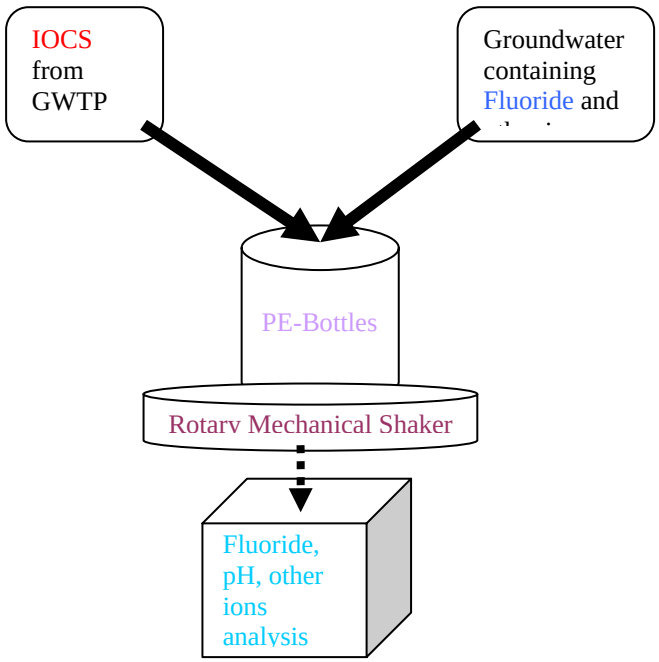
Various literatures and findings suggested that conventional technologies could not consistently remove fluoride from ground water to the recommended standards. Research obtained from Rift Valley of Ethiopia also revelled that the Defloridation plants were being operated very poorly and that the following limitation were observed-very short runs; too much caustic soda used due to adsorption of short cycles; extremely low water pH which lowered the capacity of the alumina by one half; etc. Due to the physiochemical characteristics (higher surface area and porosity) of Iron Oxide Coated Sand, it is believed that fluoride will be adsorbed from groundwater/model water.

- **The sites of iron removal groundwater treatment plants that produce Iron Oxide Coated Sand were traced in and near by the Ethiopian Rift. These are:**

  Afar region, South west Ethiopia (Awassa, Yrgalem, Dilla, Jimma, Agaro, etc.), Nazreth , Mojo, Debere Zeit, Methara, Dire Dewa and Northern part of Ethiopia were suggested.
  Field work is required in order to collect the samples from the mentioned areas.

- **Batch adsorption experimental set up and process condition were determined**

Except for the pH, bicarbonate and adsorption isotherm tests, the batch experiments can be conducted using polyethylene bottles (500 ml capacity) with mechanical round shaker operated at 300 revolutions per minutes (rpm). The schematic diagram for batch experimental set up is shown in the figure below.



Schematic diagram for batch adsorption experimental set up

All experiments will be done in duplicate at room temperature 20 ± 2 ^{o}C. The pH values will be adjusted with NaOH and HCl as appropriate. The pH range 4 to 10 will be used. Control experiments will be carried out for each set of experiments.

3. Training activities

A) Source, genesis and distribution investigation

As stated in the project document, one Ph.D. student each for the origin and defluoridation research is scheduled. The curriculum vitae (CV) of **Mr. Zenaw Tessema** of the origin part of the research team have been submitted along with the project document and also separately. If he is accepted, he will be working in the origin part of the research, which a specific sub-project proposal will be developed immediately.

B) Adsorption investigation using aluminium hydroxide

- Three MSc. students are working on this project
  - Removal of fluoride from water using granular aluminium hydroxide: adsorption in a fixed-bed column (September, 2005 – June, 2006) - Eyobel Mulugeta Damte
  - Removal of excess fluoride from water using waste residue from alum manufacturing process (September, 2005 – June, 2006) - Worku Nigussie Gugssa
  - Optimization of fluoride removal from water in a fixed bed adsorption column: pilot study (June, 2006 – December, 2006) Yoseph Abebe

- The CV of a proposed Ph. D. student (Mr. Beneberu Shimelis Feleke) has been submitted and if he is accepted, we will immediately develop a proposal for his work.

C) Adsorption investigation using clays

- One MSc. student (Mr. Ahmedin Hassen) is working on identification, characterization and modification of Clay adsorbent for Fluoride removal from Rift Valley Water. The thesis will be finalized in November 2006.
- The CV of a proposed Ph. D. student (Beneberu Shimelis Feleke) has been submitted and if he is accepted, we will immediately develop a proposal for his work.

D) Adsorption investigation using iron oxide coated sand

Due to the expected short-lived nature, no training activity has been scheduled along with this part of the research.

4. Scheduled activities for the next six months

A) Source, genesis and distribution investigation

Due to some delays entertained in the initial phases of the project, the plan for the next six months of is ambitious because it is planned to complete what has been initially planned for the year. The scheduled activities include:

- Complete data gathering, compilation, entry and map digitisation from various sources (till end of August, 2006);
- The status of fluoride project will be presented on a National Workshop on Excess Fluoride Problem in the Rift, which is organised by the Ethiopian Science and Technology Agency and in collaboration with the National Defluoridation Steering Committee;
- The information obtained from the international literature will be integrated with that of the local ones;
- Forward purchase requisition after contacting both local and international dealers and suppliers (before November, 2006).
- Processing data, and attempting hydrochemical / hydrogeological modelling, interpretational work (September, October);
- Report writing (October, November, 2006);
- Publishing the preliminary results (December-January); and
- Undertaking the 1st field work on identified area(s) for further detailed research (December / January, 2006).

B) Adsorption investigation using aluminium hydroxide

- Complete remain work regarding fluoride adsorption on to aluminium hydroxide such as detailed characterization of the adsorbent and optimization;
- Complete kinetic and thermodynamic study on the adsorption of fluoride onto waste residue from aluminium sulphate manufacturing process. The adsorption experiments conducted so far indicated that the minimum capacity of the residue is 0.1918 mg F^-/g of the media; and
- Complete literature survey report.

C) Adsorption investigation using clays

- Two additional clay samples will be investigated;
- The effect of pH, initial concentration of Fluoride on the adsorption capacity will be studied;
- The adsorption kinetics for the most appropriate clay type will be developed;
- Laboratory scale column will be designed and an optimum operation condition will be established; and
- Literature survey on clay will be finalized.

D) Adsorption investigation using iron oxide coated sand

It is planned to complete this part of the research and present the results at the next meeting in Djibouti if the financial request is approved soon. Hence, field, laboratory and processing activities are planned.

D1. Field activities

- IOCS will be collected from iron removal ground water treatment plants
- Fluoride containing real water samples will be collected from different areas particularly from the Rift, which has access for iron removal ground water treatment plant

Schedule and Budget break down for the field work (defluoridation using iron oxide coated sand)

Activities	**Time Frame, 2006**	**Requested budget (Birr) per item**	**Total Requested budget (Birr)**
Field work / for collecting iron oxide coated sand	Aug. 15-Sep 30	- ***Per diam***: Principal investigator & Assistant = 200 /d/person for 20 days - ***Vehicle rental*** = 1,000/day	**8,000** (200 X 2 X 20 Days) **20,000** (1,000 X 20 days)
Sub-total			**28,000**
Overhead cost ~ 5%			**1,400**
Total			**29,400**

D2. Preparatory works

- ☞ Grain size distribution and sieve analysis for IOCS
- ☞ Surface extraction of IOCS
- ☞ Stock solution and model water preparation

D3. Experimental set up and process condition

- ☞ Separate set of batch adsorption experiments
- ☞ Adsorption isotherms and kinetics
- ☞ pH-adsorption edge experiments
- ☞ Assess the factors that influence the adsorption capacity

D4. Data analysis and interpretation

- ☞ Compare the results with other findings and standards
- ☞ Interpreter the data using scientific explanation

D5. Write up, presentation and submission the final report

- ☞ The finding will be ready to present in Djibouti meeting

5. Purchases related

A) Source, genesis and distribution investigation

The costs of the local purchase items are given in Birr while those to be purchased from abroad are coated in EURO. We will forward purchase request after contacting both local and international dealers and suppliers.

The table below depicts the planned financial requirement for the **next six months** together with the timetable of activities.

Type of Expenses	**Description**	**Sub-T. EUR**
1. A brief overview field work for 5 days (August, 2006)	• Car rental (600 Birr / D), • Fuel (300 Birr / day), • Allowances for two researchers and a driver at 200 Birr/day basis • Communications 300 Birr	**7,800 Birr**
2. Modelling work in France – 2 researchers in collaboration with Prof. Moumtaz Razack (September/October, 2006)	2 researchers, 1m/m ea (Mr. Zenaw Tessema and Dr. Berhanu Gizaw)	**10,000 EUR**
3. Costs Related to Analyses, Required Equipment & Accessories (before November, 2006)		
Stationary (CD-ROM, DVD-ROM, writing pads, etc)		500 Birr
Photo (video) films, development and printing		500 Birr
Small ring and laminating binding machines and spares	1	5,800 Birr
Staplers (big, small) and their staples		500 Birr
Water analyses control samples cost		5000 Birr
Printing papers	30 pk x 32	960 Birr
Communication	300 / month basis for 4 months	1200 Birr
Sampling polyethylene and rock sacks		500 EUR
Fluoride electrodes	2	1000 EUR
Global Positioning System (GPS)	1	500 EUR
Dipper for water level measurement	1	500 EUR
Field Geochemical Kit	4 in one pH/Eh/Cond/Dis.O2 meter, WTW, TDS, Silica kit, micro-pipette, micro-burette, etc)	5000 EUR
AquaChem	Waterloo Hydrology, Canada – Upgrading to V5	295 EUR
Aquatest Pro	Waterloo Hydrology, Canada – Upgrading to V4	295 EUR
GDManager Edu Kit for high T/P	• 2 licenses- 15,000 EUR; • Training charge for 10 days 5,000 EUR; • Trainee cost for 15 days – 5000 EUR	25,000 EUR
4. Field Work Allowances (December, 2006)		
a) Field allowances • Dr. Berhanu Gizaw and Mr. Zenaw Tessema 1 month filed work (distribution, genesis...) • Daily Labourers (2)	30 days x 2 ea x 200 Birr = 12,000 30 days x 2 ea. x 25 Birr = 1500	13,500 Birr
b) Car rental, fuel, oil and maintenance	At a reasonable estimate of 1,100 Birr /d basis for 30 days	33,000 Birr
c) Reserve	About 100 Birr / day basis	3,000 Birr
Total filed expenses		**49,500 Birr**
Overall Total **71,760 Birr** for local expenses (about 7,000 EUR) and **43,090 EUR** for expenses in abroad and materials from abroad, which totals up to about **50,000 EUR**		

B) Adsorption investigation using aluminium hydroxide

- We are trying to get Performa invoice for some items from supplying agents.

C) Adsorption investigation using clays

- We are trying to get Performa invoice for some items from supplying agents.

D) Adsorption investigation using iron oxide coated sand

The following table shows the schedule and budget break down for the items to be purchased.

S. No.	**Activities**	**Time Frame, 2006**	**Requested budget (Birr) per item**	**Total Requested budget (Birr)**	**Remarks**
1	Cost related to analyses, required equipment and accessories	Aug 25–Oct 15			
	2.1. Lab accessories and consumables for chemical analysis of samples		PE Bottles (300 Euro), Filter (250 Euro), Syringes (40 Euro), Plastic tube (25 Euro), PE caps (35 Euro), Reagents (500 Euro), shaker (650 Euro)	18,000	
	2.2. Material characterization and water quality analysis		Lab fee, (17.5/sample X 20 sample)	3,500	To be paid to A.A. Water and Sewage authority lab
	2.3. Stationeries and accessories			1,000	
	2.4. Photo films and development		8 Euro per film X 10 Film	800	
	2.5. Binding, Photocopy, etc			1,000	
Sub-total				**24,300**	
Over head cost ~ 5%				1,215	
Grand Total budget			**25,515**		
2	Writ up and submission	Oct 16-Nov 5		-----	

N. B. The Budget should be released as soon as possible (1st half of August, 2006). All spending will be made locally.

6. Conclusions and Recommendations

As briefly summarised in the document, by in-large, the fluoride project is progressing as planned. Smooth communication and understanding amongst researchers and facilitators have been the key factors for this and hence it is important to keep up the momentum.

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