Neutralization Of Highly Alkaline Waste Streams Of Estonian Oil Shale Thermal Processing

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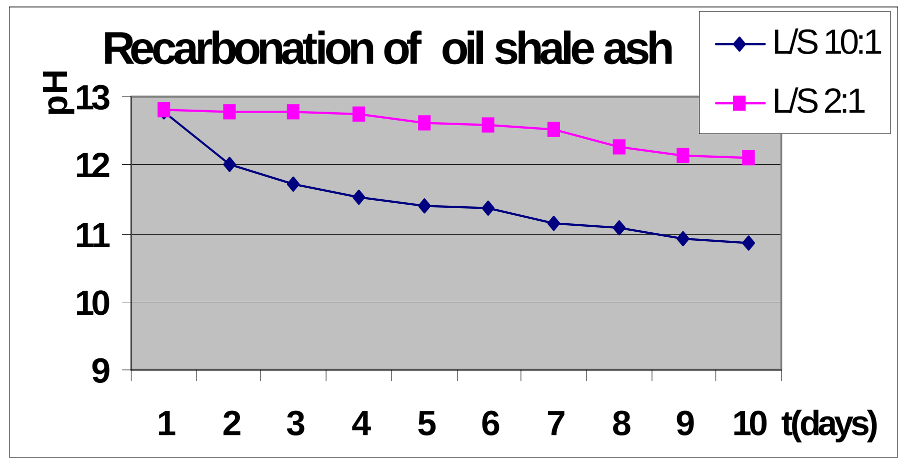
It is well known that changes occur in oil shale ash and retorted oil shale upon disposal. The reduction in pH is observed in leachates upon exposure to an environment. pH reduction has been attributed mainly to recarbonation and also to oxidation of reduced sulfur in retorted oil shale. We have studied natural recarbonation of semicoke. We have also studied recarbonation of oil shale ash and coke-ash residue from solid heat carrier process of shale oil production and leachates of these wastes.

Old semicoke embankment and the area around it, which is used as a semicoke landfill today.

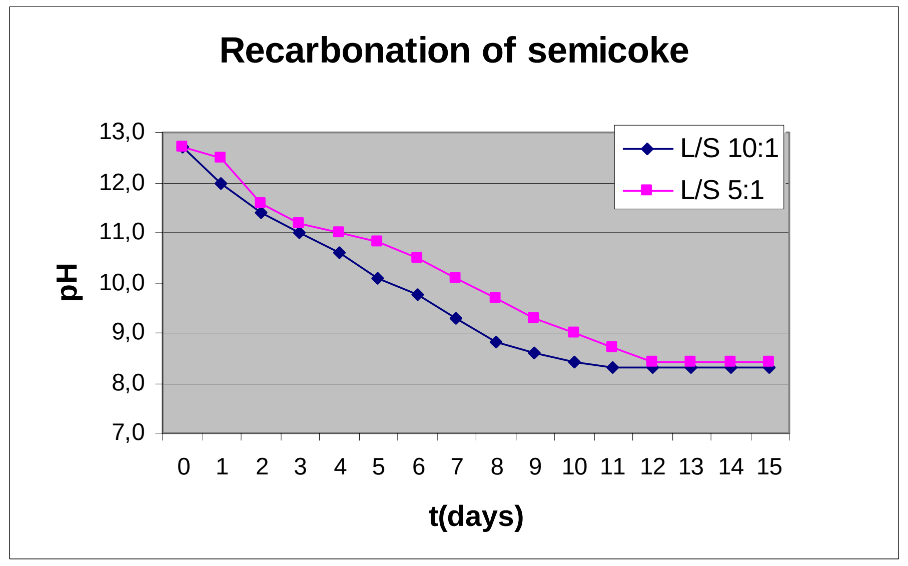
Leaching and natural recarbonation give a pH drop in the upper layer. It takes several years till the soil is suitable for plant growth.

Birch (*Betula pendula*) is planted as a pioneer species.

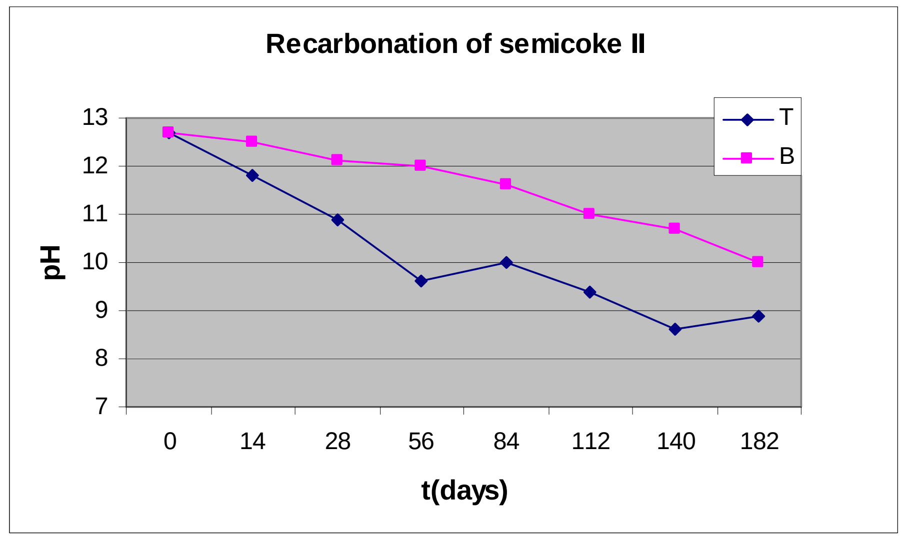
Photos: Kiviõli, Estonia



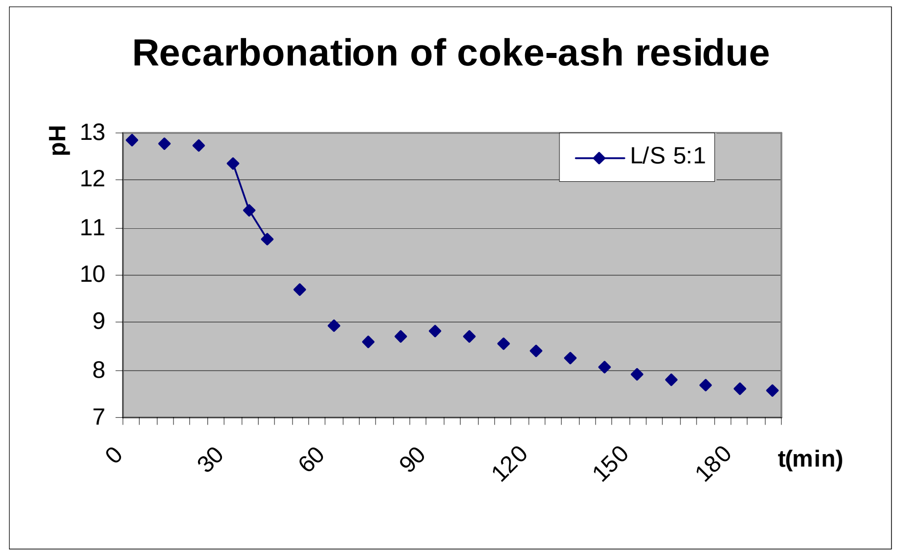
Series of laboratory experiments were performed with combustion ash to mimic enhanced natural recarbonation, Distilled water was added to ash and the samples were kept in a open glass cylinder on a mixer (ca 100 rpm). Water was added daily to maintain the liquid-solid ratio.



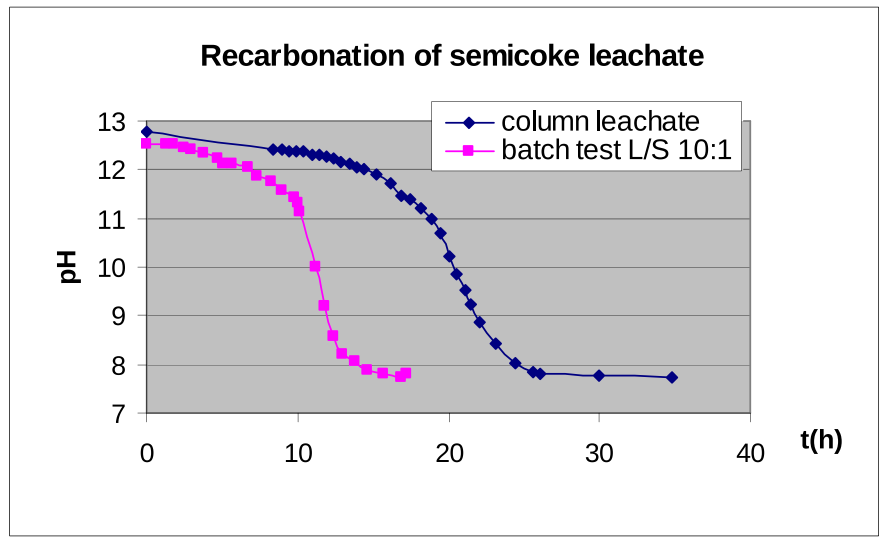
Laboratory and field experiments were performed with fresh semicoke to study natural and enhanced natural recarbonation. Figure illustrates pH drop in laboratory experiments, which were performed in the same way as experiments with ash. pH drop to 8,3 is achieved in less than 2 weeks.



Recarbonation of semicoke was studied in field conditions on two test plots. Figure illustrates change in pH of the leachates originating from samples collected from the upper 5 cm (T) and lower 5cm (B) layer of the plot with leachate drain in the bottom. (1)



Laboratory experiments were performed to characterize recarbonation of ash residue of Galoter process. Figure illustrates pH drop in the enhanced recarbonation experiment with carbon dioxide (flow 10l/l/h). Very intensive hydrogene sulfide emission takes place when pH drops to 8,5.

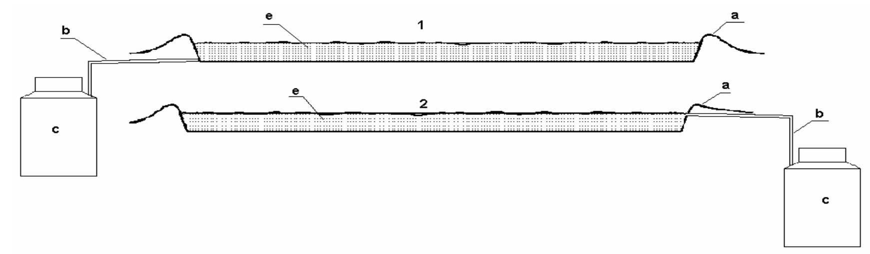


Recarbonation of alkaline leachates was studied in laboratory and field experiments. Figure illustrates pH drop of leachates mixed in a glass cylinder in laboratory experiments.

Changes in the leachate composition of recarbonated semicoke.

	Semicoke	L/S =10l/kg		L/S=10l/kg		L/S=2l/kg		Precipitate
	mg/kg	Amount leached mg/k		Amount in the leachate mg/l				mg/kg
Component	**27**	**27**	**27R**	**27**	**27LR**	**27**	**27 LR**	**27LRP**
Ca	250000	9800	8800	980	350	2200	1500	390000
Mg	12000	0,17	2000	0,017	0,1	0,046	0,12	7,0
Fe	25000	<0,2	<0,2	< 0,02				9,4
Na	1100	230	170	23	19	94	70	84
K	8800	1700	1200	170	180	940	880	700
Al	16000	<0,2	0,37	< 0,02				
As	10	<0,1	<0,1	< 0,01				
Ba	54	3,1	0,26	0,31	0,49	0,97	0,82	
Cr	18	<0,2	<0,2	< 0,02				
Cu	10	<0,2	<0,2	< 0,02				
Mn	230	<0,2	0,54	< 0,02				
Mo	4,5	0,44	0,92	0,044	0,049	0,11	0,11	
Ni	17	<0,2	<0,2	< 0,02				
Pb	39	<0,2	<0,2	< 0,02				
Zn	13	<0,2	0,48	< 0,02				
Sr	300	51	9,3	5,1				340
S total	28000	4600	17000	460	460	2100	1900	4200

Elements present in eluates were analysed using an ICP-AES method. The composition of semicoke and precipitate formed during recarbonation are olso given in the table. Standard batch tests were performed with liquid ratio 10 and 2 l/kg. L=leachate;R=recarbonated;



Construction of test plots and a scheme showing different possibilities for leachate collection

Natural recarbonation can be used as a method for treatment of semicoke. Unfortunately the territory needed for deposition “in thin layer” and handling of the water balance of the landfill will be too expensive. Nevertheless, this approach can be used when a quick mineralization and drop in pH is needed. For example during preparation of material for closure of old semicoke landfills.
Recarbonation can be an essential part of the treatment of semicoke landfill leachate and other alkaline waste waters of oil shale thermal treatment.
The results of the present investigation can be used to predict the leaching behavior of alkaline wastes of oil shale thermal treatment upon deposition and weathering.
When flue gases or acids will be used for neutralization of alkaline waste streams from retorting, hydrogen sulfide emissions from wastes containing reduced sulfur should be taken into account.