Stellingen

Behorende bij het proefschrift
"Selective Separation of very Small Particles by Flotation
in relation to Soil and Sediment Remediation"
van Huib Mulleneers
Wageningen, 19 oktober 2001

1. De ontwikkelde flotatiemethode is in staat om ook zeer kleine hydrofobe en hydrofiele deeltjes (2-25 µm) van elkaar te scheiden en de invloed van entrainment te minimaliseren.

   Dit proefschrift (hfst 5)

2. Collector noch promotor hebben een positieve invloed op de reiniging van de in dit onderzoek gebruikte baggerspecie.

   Dit proefschrift (hfst 4, 6 en 7)

3. Het gebruik van een scheidingscoëfficiënt (CS) naast de in de mijnbouw gebruikelijke termen als grade en recovery, vergroot de transparantie van de flotatieresultaten niet, zeker niet als ook nog de definitie van CS ontbreekt.

   Niewiadomski, M. et al (1999). Fuel 78 (2): 161-168.

4. Bij onderzoek naar de "Franse paradox" worden cultuur- en klimaatverschillen veelal buiten beschouwing gelaten en de invloed van anti-oxidanten als in rode wijn zwaar overschat.

5. Hoewel een slechte economische situatie een milieuvriendelijke levenswijze in de weg staat, leidt bij veel mensen juist een verbeterde economische situatie tot het verdwijnen van milieu-idealen.

6. Het samenvoegen van Milieutechnologie en Landbouwtechniek in een nieuwe studierichting is even onlogisch als de hele Friese propedeuse.

7. Counteren is de meest aanvallende voetbalspeelstijl.

Selective Separation of very small Particles by Flotation

in Relation to Soil and Sediment Remediation

Huib Mulleneers

Promotor

Prof. dr. ir. W.H. Rulkens
Hoogleraar in de milieutechnologie

Co-promotoren

Dr. ir. L.K. Koopal
Universitair docent bij het laboratorium voor Fysische Chemie en Kolloïdkunde
Dr. ir. H. Bruning
Universitair docent bij de Sectie Milieutechnologie.

Samenstelling Promotiecommissie

Prof. dr. A.T. Maes	Katholieke Universiteit Leuven
Prof. dr. ir. S.E.A.T.M. van der Zee	Wageningen Universiteit
Dr. ir. J. Bovendeur	AVR Milieutechniek, Waalwijk
Dr. ir. K.P. Groen	RIZA, Lelystad

Selective Separation of very small Particles by Flotation

in Relation to Soil and Sediment Remediation

Huib Mulleneers

Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit,
Prof. dr. ir. L. Speelman,
in het openbaar te verdedigen
op vrijdag 19 oktober 2001
des ochtends te elf uur in de Aula.

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Author: Mulleneers, H.A.E.
Title: Selective Separation of very small Particles by Flotation in Relation to Soil and Sediment Remediation
ISBN: 90-5808-505-8
Publication Year: 2001

Thesis Wageningen University, Wageningen, the Netherlands – With references – with summary in Dutch - 117 p.

Abstract

Mulleneers, H.A.E. 2001. Selective Separation of very small Particles by Flotation in Relation to Soil and Sediment Remediation. PhD-thesis, Wageningen University, 117 pages.

Next to numerous contaminated sites, also large quantities of polluted dredged sediments have to be cleaned in the near future in the Netherlands. Soil washing (classification) is one of the most common remediation techniques to remediate contaminated dredged sediment and excavated soil. It uses chemical and physical particle properties to separate contaminated particles from clean particles. The process is less successful when a large fraction of soil particles smaller than 63 µm is present (the fines), which is very likely in dredged sediments. Classification is also not suitable when polluted and clean particles hardly differ in density or size.

In cases where classification techniques fails, flotation can be a successful alternative remediation technique. Flotation is a separation technique based on the capture of particles by bubbles and their collection in a froth layer. It can also be used to succeed the classification techniques in order to clean the fines fraction.

Also in flotation the separation of small particles cause problems. Factors like entrapment and entrainment lead to reduction in efficiency. Entrapment problems occur when fine hydrophilic particles become physically trapped by hydrophobic particles or bubble-particle aggregates. Hydraulic entrainment occurs when hydrophilic particles are recovered in the liquid film between air and bubbles in the froth. Entrainment becomes prominent when large quantities of fine particles are treated.

This thesis investigates the possibility of the selective separation of very small particles by flotation in relation to the remediation of contaminated soil and sediment. The influence of some flotation reagents is investigated and the importance of the contact angle is studied.

A new flotation device was developed which uses dissolved air, as small bubble source, together with a sedimentation zone. The mixing and sedimentation zone are separated by a baffle to prevent settled particles falling back into the mixing zone. This creates a flotation reactor that is capable of separating even the smallest particles whilst minimizing the effects of entrainment and entrapment. For contaminated soil it means that when the contamination is present in a hydrophobic fraction and the other fractions consists out of clean hydrophilic particles, there is no limitation for the separation of these particles by flotation.

The new flotation technique was used to clean fractions of contaminated soil and sediment. The remediation of a sandy soil sludge contaminated with PAH was very successful and PAH removal could be further increased with flotation agents as Diesel and Montanol. The fraction of 45-90 µm of PAH contaminated dredged sediment from Overschie and the Petrol Harbor was also successfully treated with flotation. The remediation was less efficient for the smallest fractions (<32 µm) of these sediments, but PAH was still selectively removed.

The counter current flotation sedimentation cell is a practical tool to perform a quick laboratory test to investigate if contaminated soil or sediment could be remediated by flotation. Next to that, on basis of the laboratory experiments a prototype reactor could be developed to remediate even the smallest fractions of contaminated soil and sediment in practice. The flotation reactor could succeed other classification processes, but could also be applied as a single (mobile) remediation step. Moreover, this new developed flotation process might even be more useful to selectively float more valuable particles or powders in other industrial fields.

Abstract
Content

Chapter 1 General Introduction 1

Chapter 2 Flotation 11

Chapter 3 Flotation of Soot Particles from a Sandy Soil Sludge 29

Chapter 4 Flotation of PAH-Contaminated Dredged Sludge 43

Chapter 5 Selective Separation of Fine Particles by a New Flotation Approach 55

Chapter 6 Remediation of the Finest fraction of Dredged Sediment by Flotation 69

Chapter 7 Discussion 85

Summary 95
Samenvatting 101
References 107
Dankwoord 115
Currucilum Vitae 116
Publication List 117

1

General Introduction

1.1 Introduction

1.1.1 Contaminated Soil

Quality of water and air have always been of great human interest. The soil quality however, has only recently been regarded as source of concern. Before, soil was mostly regarded as indestructible (Henkens 1994).

For the Netherlands, the concerns started in the late seventies and the early eighties, with the discovery of several extremely polluted sites. First estimations suggested around a few hundred, but later investigations indicated that maybe more than 100.000 sites were polluted with all kinds of chemicals (Rulkens et al. 1994).

Soil pollution can be caused by direct spills, atmospheric deposition or refuse dump sites. Typical contaminants in the soil are heavy metals, Polycyclic Aromatic Hydrocarbons (PAH), Pesticides and mineral oil. Besides the direct risks of contaminated soil sites. It is also closely related to the groundwater quality. Contaminants in the soil can dissolve and thus pollute groundwater as well as rivers, lakes and ponds. Next to that, volatile pollutants can also cause problems to the health of humans and animals. Due to the high risk of contaminated soil to human health and ecosystems, polluted sites have to be remediated.

At the moment the Dutch Ministry of Housing Spatial Planning and the Environment (VROM) located around 60.000 sites which need urgent clean up (VROM 2001).

1.1.2 Contaminated Sediment

Transport over water is of major importance for the Dutch economy. Free waterways and harbors are thus simply necessary. Therefore, waterways need regularly dredging to remove settled fine slimy material and thus to obtain good navigability. Also watermanagement, to maintain a proper water run-off, results in removal of sediment .

Dredged sludge always was an useful agricultural product and used to be spread over land to improve soil quality. This is changed in the early eighties with the discovery of contaminants in the dredged sediment (AKWA 2001). The settled fine material often contains contaminants like heavy metals and PAH caused by upstream industries, atmospheric deposition or direct spills. Sometimes the sediment is so polluted that it has to be removed for environmental reasons.

It is estimated that till 2010 425 million cubic meters and till 2015 around one billion cubic meters of sediment have to be dredged. Around a quarter of this dredged sludge will be slightly to heavily contaminated (Groen 1999; AKWA 2001).

1.2 Polycyclic Aromatic Hydrocarbons

1.2.1 Introduction

One group of the contaminants in the soil and sediment are Polycyclic Aromatic Hydrocarbons (PAH). PAH arise from uncompleted combustion of oil, coal, wood or other organic molecules. Sources of PAH can be natural and anthropogenic. Natural PAH sources are for example forest fires, volcano eruptions and syntheses of PAH by microorganisms en plants (Visschers et al. 1988).

PAH are characterized by the presence of two or more aromatic hydrocarbons. The number of different PAH is extremely large and impossible to distinguish. Therefore standard series are defined by the EPA and also by VROM. The 16 EPA-PAH and the 10 VROM-PAH are presented in figure 1.1.

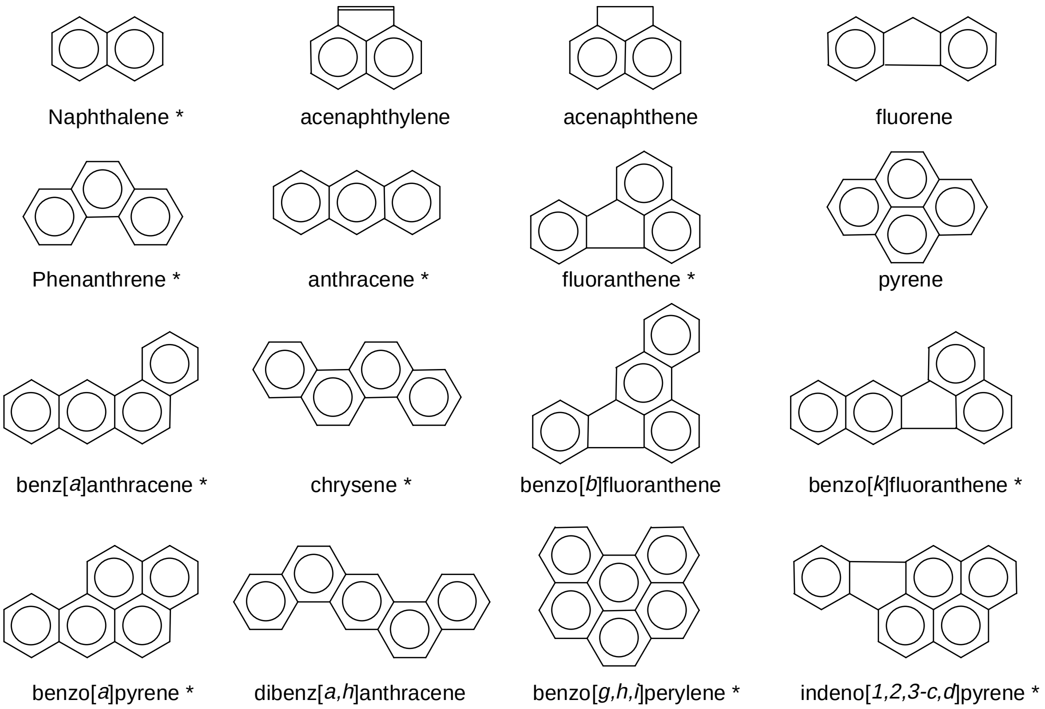


Figure 1.1 *Chemical structures of the 16 EPA-PAH, the 10 VROM-PAH are marked by **

The natural background values of PAH are in the range of 1 to 1300 µg/kg d.m.. PAH contamination of soil is often high at former gas plants and in areas were charcoal is used (Visschers and Verschueren 1988; Henner et al. 1999).

1.2.2 Toxicity of PAH

Already since 1775 PAH are suspected to be toxic. At that time the English doctor, Percival Potts, mentioned the high number of scrotum cancer for London chimney sweepers. Nowadays there is scientific proof that aromatic compounds like dibenz[a,h]anthracene en benzo[a]pyrene induce cancer and are toxic for plants (Slims et al. 1983; Engbertsen et al. 1988; Visschers and Verschueren 1988)

Carcinogenic activity of PAH is not caused by the toxicity of the PAH itself. It is accepted that in living organisms PAH are transferred into more reactive and toxic compounds as for example 7,8-dihydriol-9,10-epoxide. This epoxide is less easy detoxified and therefore longer in the body and can interact by covalent bindings with DNA, inducing cancer (Engbertsen and Groot 1988).

1.3 Dutch Soil Remediation Policy

Principle in the laws around soil pollution is that the ones responsible for the pollution have to pay for the remediation “de vervuiler betaald” (VROM 2001). However, often the polluter cannot be traced or the pollution is from too many years ago.

At the moment approximately 1,2 billion guilders is spent on soil remediation in the Netherlands every year. One third of it was paid by the private sector and industries, slightly more than one third by the national government and the rest by the local government (VROM 2001).

Until 1997 Dutch legislation was based on multifunctionality of the soil after remediation. Because of a stagnation in remediation operations, in 1997 a new approach was chosen, based on functionality and cost effectiveness. The old A-B-C values of polluted soil were changed into more practical “target” and “intervention” values. When all the contaminant concentrations are under the target value the soil is regarded clean. When the concentration of a single contaminant is above the intervention value, the soil is regarded polluted (VROM 2000).

When after remediation soil is used for construction purposes it has to fulfill to the standards of the law of construction materials (CUR 1999). When soil is not re-used but dumped there has to be paid a penalty fee. The intervention and target values and the values for construction materials on behalf of PAH are given in table 1.1.

Table 1.1 Target, intervention and "construction" values of PAH for contaminated soil.

	target value mg/kg d.m.*	intervention value mg/kg d.m.*	construction value mg/kg d.m.*
Naphtalene	-	-	5
Phenantrene	-	-	20
Anthracene	-	-	10
Fluoranthene	-	-	35
Benz[a]anthracene	-	-	40
Chrysene	-	-	10
Benzo[k]fluoranthene	-	-	40
Benzo[a]pyrene	-	-	10
Benzo[g,h,I]perylene	-	-	40
Indeno[1,2,3-c,d]pyrene	-	-	40
Total (sum 10 PAH)	1	40	40

*Values are for standard soils up to 10% organic matter. When the organic matter content is between 10% and 30% the values are corrected by multiplying by (%organic matter/10).

For dredged sediments other restriction are involved. Clean up of contaminated sediment is mostly not paid by the polluter but shifted on to for example the harbor master (Ende et al. 2001). Till now, contrary to contaminated soil, there is no penalty for dumping contaminated dredged sediment. But in the near future there will be a tax for dumping contaminated sediment with a sand content of around more than 60% (Jawalapersad 2001). For dredged sediments there are target, limit, test and intervention values (VW 2000). The values for PAH for dredged (fresh water) sediment are presented in table 1.2.

Table 1.2 Target, limit, test and intervention values of PAH for dredged sediment (fresh).

	target value mg/kg d.m.*	limit value mg/kg d.m*	test value mg/kg d.m.*	intervention value mg/kg d.m.*
Sum 10 (VROM-PAH)	1	1	10	40

*Values are for standard soils up to 10% organic matter. When the organic matter content is between 10% and 30% the values are corrected by multiplying by (%organic matter/10).

From these values contaminated sediments are divided in 5 different classes (Gorree 1995). The classification for PAH is given in table 1.3.

Table 1.3 Classification of contaminated sediment with PAH values and restrictions

Class	Value	Application
0	< target	no restriction
1	target – limit	spreading under certain restrictions
2	limit – test	spreading under certain restrictions
3	test – intervention	no spreading except some exceptions
4	> intervention	spreading is forbidden

1.4 Remediation technologies

1.4.1 Introduction

Remediation of contaminated soil can be performed using in-situ and/or ex-situ techniques. Remediation techniques can be biological, physical or chemical. With in-situ techniques the site is cleaned without removing the soil. The most common in-situ technique is pumping and cleaning the groundwater (pump and treat method). With ex-situ techniques the soil is excavated and treated on-site or in a plant elsewhere. For ex-situ remediation several remediation techniques are available like, solvent extraction, phytoremediation, immobilization, biological treatment, thermal treatment, and soil washing/ classification techniques.

Solvent extraction removes pollutants from soil by extracting and concentrating the contamination in a solvent (Rulkens et al. 1998).

In phytoremediation, plants are used to extract the contaminants from the substrate to their vegetative parts. The crops are then harvested and incinerated (Leeson et al. 1999).

To reduce the risk of the pollution immobilization can be applied. With immobilization contaminants are encapsulated for example in granulates by which the contamination is excluded from the environment (Plette et al. 1999).

Biological treatment might be the mostly studied technique. Biodegradation uses bacteria or fungi to remove contaminants in soil. A lot of bacteria and fungi are able to use contaminants as substrate or co-substrate and thereby removing the contamination from the soil (Cassidy et al. 1997; Agteren et al. 1998; Kotterman 1998; Doelman et al. 1999; Ferdinandy 1999).

In thermal treatment soil is heated to 400-800^{o}C depending on the contamination. At these temperatures organic pollutants will decompose or evaporate. Evaporated gasses might need an extra incineration step to remove toxic components (RIZA 1998).

Classification techniques use chemical en physical particle properties to separate contaminated particles from the clean sandy soil (Werther et al. 1990; Neesse et al. 1991; Feenstra et al. 1995). Soil washing and problems with the fines are further described in the next paragraph.

Also other techniques like magnetic separation through pipelines are used to clean contaminated soil (Hendriksen 2000).

1.4.1 Soil Washing

Soil washing is one of the most used remediation technique (VvAV 1997). Many remediation plants are in operation and clean tons of contaminated soil. The common procedure in soil washing is the separation of contaminated fractions from the clean sandy soil by classification techniques. An overview of a soil washing plant is given in figure 1.2.

Figure 1.2 *Flow sheet of a soil washing plant*

In general a soil washing plant firstly removes the physical contaminants as for example wood, plastics, stones and other larger objects. A magnetic separator might remove the iron and other magnetic particles. The remaining soil is then transformed in a slurry by adding process water and classification techniques like hydrocyclones (figure 1.3), spirals, and upstream columns follow. Sometimes the classification techniques are preceded by processes

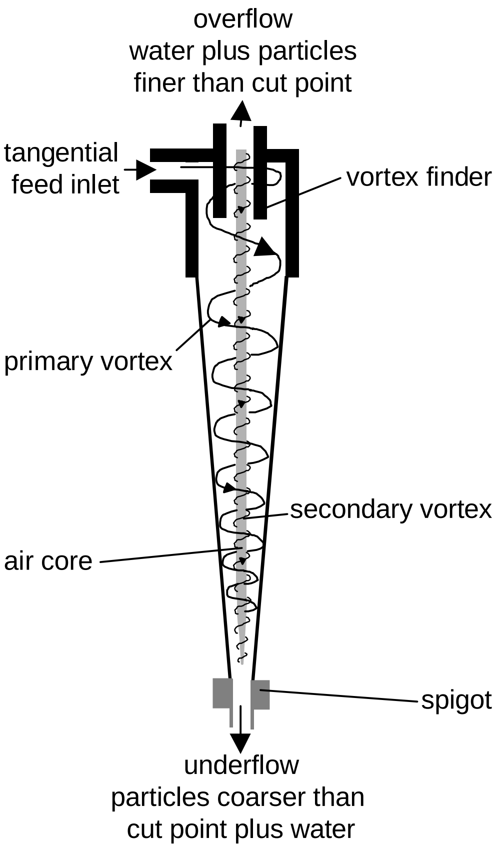


Figure 1.3 *Schematic drawing of a Mozley hydrocyclone*

like grinding or high pressure water treatment, to liberate aggregates. The classification techniques try to separate the clean sand fraction from the lighter or heavier contaminated particles. After classification the sandy soil sludge is divided into a sand fraction (> 63 µm) and contaminated fractions. The main contaminated fraction is mostly the fines fraction.

The sand fraction might be clean but it can also still be contaminated by for example larger hydrophobic soot particles. Flotation techniques are often used to remove those contaminants in the sand fraction. Flotation is separation technique based besides size and density, on the surface chemistry of particles. Flotation techniques will be extensively discussed in chapter 2. The process is finished with dewatering processes.

A problem with soil washing is the large volumes of fines which can remain when treating contaminated soil with high amounts of fine sand, silt and clay. Further treatment of these fines is therefore recommended. It is of economic importance, but also in environmental point of view, necessary to find new techniques to clean these fines. Therefore, in this study one of the most promising techniques to treat these fines, the flotation separation process, is investigated.

1.4.2 Remediation of Dredged Sediments

Because of the different laws for dredged sediments they are less often cleaned than contaminated soil. Only simple sand separation techniques are sometimes used for sediments with a sand fraction of more than 60%. Simple sand separation occurs with large tilted basins where the sand fraction is separated from the lower settling fines. A problem occurring with simple sand separation is that it does not remove the physical contaminants like plastic bottles and stones. Reuse of the remaining sand is therefore very unlikely. After sand separation the remaining fines are dumped in deposits. When the sand fraction is lower than 50% dredged sludge is not treated at all and directly dumped in deposits like the Slufter, Papegaaijenbek, or the IJsseloog. The deposits are far from sustainable. Already at the moment there are many problems with the position of deposits and also most deposits need maintenance till end of days to prevent the spreading of the contamination in the ecosystem.

Ripening in temporary deposits to remediate the dredged sediments might be a more promising solution for the contaminated sediment (Vermeulen et al. 2000).

When new laws are in force dredged sediment with a sand fraction of more than 60% will more often be cleaned. Soil washing is probably the most common technique to handle this problem. The problems with fines however will be significantly higher than with contaminated soil because dredged sediment is likely to contain large fine particle fractions. The need to find new technologies for these fines will therefore only be higher with the coming treatment of dredged sediments. Like mentioned before is the flotation separation technique, studied in this research, on of the most promising techniques to tackle the problems with these fines fractions.

1.5 Objective and Outline of This Thesis

The main objective of this thesis is to investigate the possibility of the selective separation of very small particles by flotation. The research is mainly focussed on the remediation of fine fractions of contaminated soil or sediment. A new flotation approach is applied. The influence of some flotation reagents is investigated and the importance of the contact angle is studied.

In chapter 2, the principles about flotation are described. Especially attention is given to dissolved air flotation and the theory of floating small particles. The theory around attachment of particles to bubbles and the influence of contact angles related to flotation is explained and an overview of the flotation reagents is given.

In chapter 3, the remediation of a fine fraction of a soot contaminated soil is studied. To investigate the behavior of the system, the effect of three different types of collectors on the static contact angles on both silica plates and soot particles is compared with the flotation recovery of soot or silica from suspensions of the pure materials. To screen the ability of the collectors in a more practical situation, some batch flotation studies are carried out using the polluted sludge fraction. Finally, the polluted sludge is treated in a semi-continuous flotation approach, to investigate the optimal flotation conditions.

In chapter 4, the 45-90 µm fraction of two different types of dredged sediment, both contaminated with PAH are studied. Petrol harbor (Amsterdam) sludge is heavily contaminated and Overschie (Rotterdam) is less contaminated. The hydrophobicity of the different particles in the absence and present of flotation reagents is investigated by contact angle measurements. Finally, possibility of cleaning of the two fractions with dissolved air flotation is tested in batch laboratory studies.

In chapter 5, The flotation device used in chapter 3 is further modified. The separation efficiency of this new flotation device is tested with small soot-like and silica particles (2-25 µm). Studies are performed on pure and mixed samples of the two different particles. flotation reagents are used and grade and recoveries are calculated.

In chapter 6, the new flotation device is used to test the remediation of the finest fractions (<32 µm) of the dredged sediments from the Petrol Harbor and Overschie. The fractions are obtained by the use of cyclones. Flotation reagents are used to improve the process and PAH removal is calculated.

Finally an overall discussion is presented in chapter 7.

2

Flotation

2.1 Flotation History

Flotation is a separation technique based on the capture of particles by bubbles and their collection in a froth layer (Kitchener 1984). Already in the 15th century there is mention of enrichment of copper carbonate by flotation. However, it emerged as a workable process only late in the 19th century as a consequence of the Industrial Revolution.

One of the most pleasing, however fictitious, story about the invention of flotation is that of miss Carrie J. Everson. This school-teacher is said to have washed some ore samples bags which had become greasy in her brother’s laboratory, and, in agitating them in the wash-tub, she noticed that the dark sulfide mineral was concentrated in the floating scum, whereas, the gangue was not (Kitchener 1984).

The real invention of the process is impossible to ascribe to any single person or date. In 1860 William Haynes patented a process in which oil was used as rising force. A similar process where bubbles, generated by boiling were used, was patented in 1877 by the Bessel brothers. This is probably the precursor to froth flotation as we know it today (Kitchener 1984; Fuerstenau 1999).The first reported laboratory studies on the froth flotation of coal were in 1915 (Ralston et al. 1922), the first plant was in operation in 1920 (Bury et al. 1920-21) in Aplan (Aplan 1999).

Flotation processes have an enormous impact on the economy of the whole industrial world. Without flotation many familiar metals and inorganic raw materials would be exceedingly scarce and costly (Kitchener 1984).

2.2 Flotation Theory

2.2.1 Principle of flotation

The principle of flotation is based, like mentioned before, on the capture of particles by bubbles and the collection of them in a froth-layer. In some cases flotation is used to float all the particles present, for example in water treatment (Ives et al. 1995). In most other cases like mineral flotation (Weiss 1985) it is used to selectively separate particles from other particles. This process of selective flotation is schematically presented in figure 2.1.

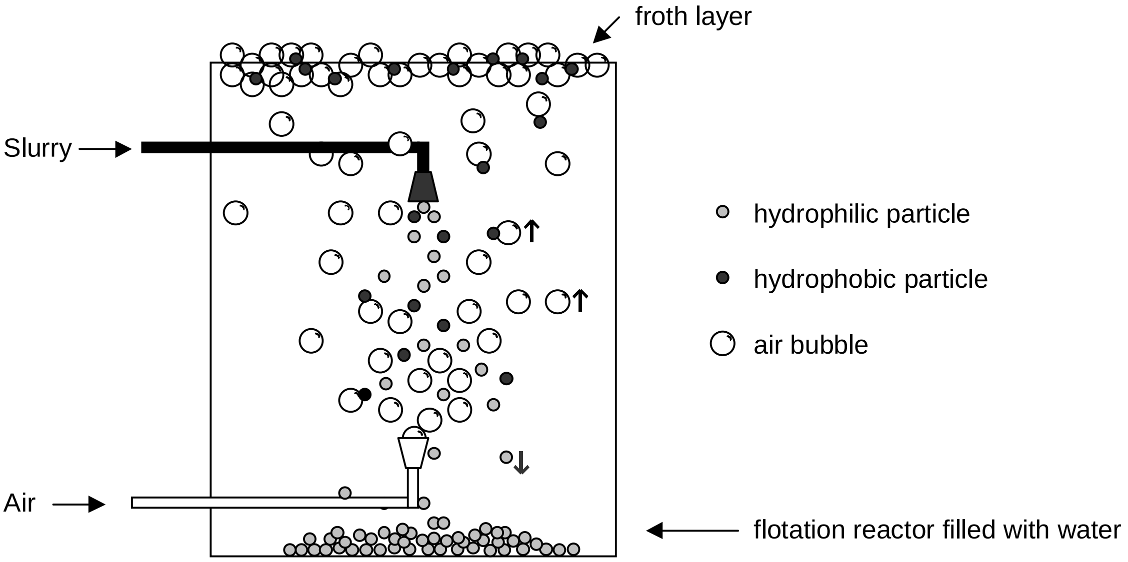


Fig 2.1 *Principle of selective flotation*

Hydrophobic particles will attach to air bubbles and float into a froth-layer, whereas hydrophilic particles do not have an affinity with the air bubbles, therefore do not attach, sink to the bottom or remain in the reactor.

2.2.2 Capture of particles by bubbles

The capture of particles by rising bubbles is the central process in froth flotation. For efficient capture to occur between a bubble and a hydrophobic particle, they must undergo a close encounter, governed by the hydrodynamics in the reactor (Ralston 1999).

The capture or collection efficiency E of a bubble and a particle can be ascribed as (Derjaguin et al. 1961)

$$E = Ec.\ Ea.Es \qquad \text{(i)}$$

Where Ec is the collision efficiency, Ea is the attachment efficiency and Es is the stability efficiency of the bubble particle aggregate. The efficiency is based on three (not discrete) zones as illustrated in fig 2.2.

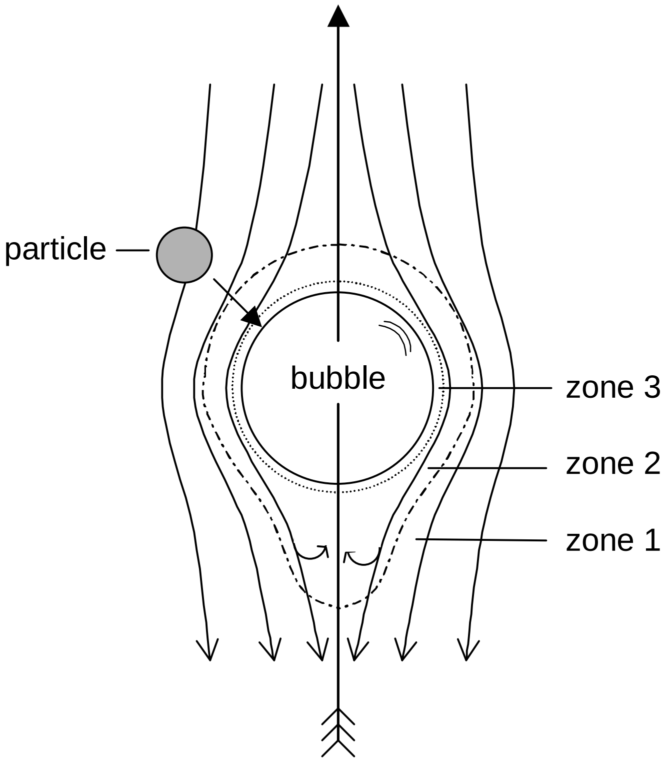


Fig 2.2 *Zones of interaction between a bubble and a particle (after Derjaguin et al 1961)*

In zone 1 the hydrodynamic forces are dominant, in zone 2 and 3 the interfacial forces and surface forces are dominant (Derjaguin and Dukhin 1961; Ralston 1999; Ralston et al. 1999). Once the particle is in the wetting zone (third zone) the fate of the particle as to whether adhesion occurs or not, is decided by three forces namely, London- van der Waals, electrostatic and structural forces. For very fine particles the structural forces might be neglected (Derjaguin et al. 1979). Yoon suggested that in addition to the forces mentioned there also might be a “hydrophobic force” that drives the process of bubble-particle adhesion (Yoon et al. 1996).

The electrostatic forces are caused by the fact that particles and bubbles in solution become charged by processes like, adsorption of potential determining ions, dissociation or association of surface active groups, isomorphic substitution, specific adsorption or adsorption of charged molecules like surfactants (Hiemenz 1977).

The London van der Waals attraction forces are always present, the most characteristic parameter being the effective hamaker contstant, mostly attractive (Hiemenz 1977).

The interaction between electric- and London van der Waals forces is known as the DLVO-theory (Derjaguin, Landau, Verweij, Overbeek) (Derjaguin et al. 1941; Verweij et al. 1948). When particles, or bubble and particle, with the similar charge approach each other they will undergo a repulsive electrostatic force and an mostly, depending on the hamaker constant, attractive van der Waals force, schematically presented in figure 2.3. The repulsive force (curve a) together with the attractive force (curve b) lead to a total force (curve c). A positive value of the sum of both forces corresponds to repulsion, a negative to attraction.

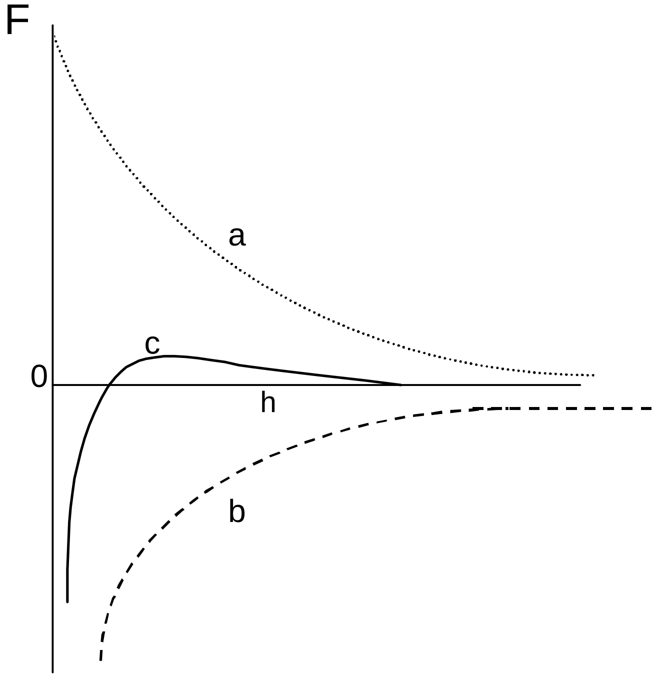


Fig 2.3 Schematic drawing of forces at distance h for a particle-particle or particle-bubble interaction with similar charge

The hydrodynamic (Fh) and gravity (Fg) forces which promote collision (Ec) of particle and bubbles can also lead to detachment of them. When detachment forces overcome the attractive forces, particle and bubble will detach and flotation will not occur. Incorporation of these conditions of both attachment and detachment into the DLVO theory leads to a "flotation domain" in which flotation is possible. Qualitatively the situation is illustrated in figure 2.4.

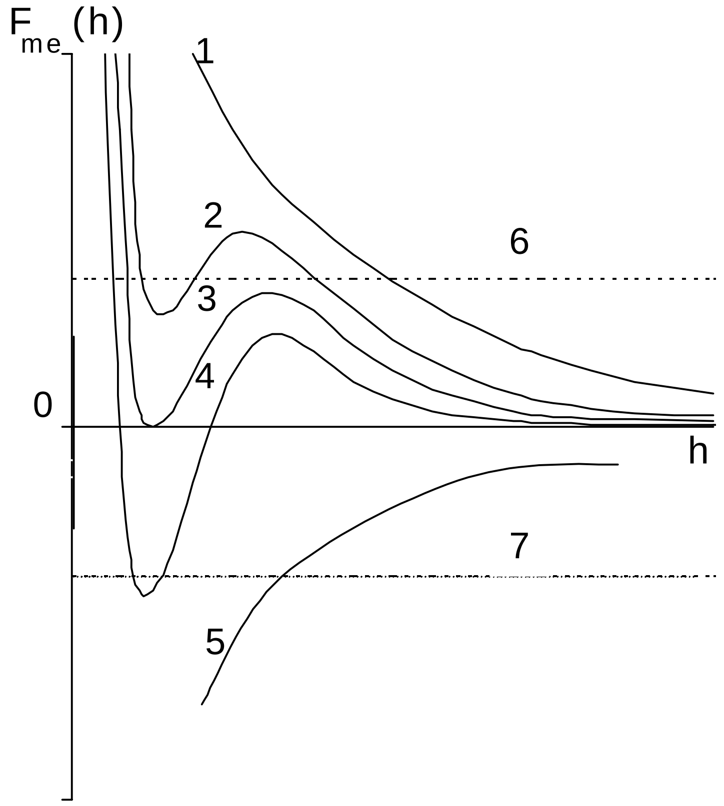


Fig 2.4 *Qualitative scheme of DLVO forces for a bubble and particle with the same sign of surface charge as a function of the shortest distance bubble and particle h (after Mischuk, 2001)*

Two different cases appear. In the first case repulsive forces exceed attraction forces at all distances and the total force is repulsive or equal to zero (curve 3). In the other cases, the attractive force dominate at certain distance (curve 4) or all distances (curve 5). The total pressing force (Fh + Fg) that presses the particle nearer to the surface is negative, however, to compare it with the surface forces it is convenient to show its value with an opposite sign (curve 6). For curves 1 and 2 the pressing force is insufficient for the formation of a bubble particle aggregate, as seen from the comparison of curve 6 and curves 1 and 2, where the barrier height is larger than the total pressing force. Even when the pressing force is large enough and the particle is pressed to the bubble surface, this does not mean that irreversible attachment occur. As the particle moves along the bubble surface, the direction of the normal component of the liquid velocity changes. When it is directed from the surface to the bulk, the total pressing turns into a detachment force. If both the total force and the total detachment force are positive, detachment occurs. Only if absolute value of the detachment force (curve 7 which is again presented with the opposite sign) is smaller than the depth of the well, the aggregate is stable and the heterocoagulation of the particle and bubble is irreversible as shown for curve 4 and 5 (Mischuk et al. 2001). Curve 5 suggest so strong attachment which does need a pressing force for example when particle and bubble are of opposite charge and electric forces also function as attraction force.

Macroscopically particle – bubble attachment can also be described (without incorperating the hydrodynamics) on the basis contact angle and wetting phenomena. The situation of partial wetting can be described by Young's law (ii).

$$\Upsilon_{sg} = \Upsilon_{sl} + \Upsilon_{lg} \cos(\theta) \qquad \text{(ii)}$$

Where Υ_{sg}, Υ_{sl} and Υ_{lg} are the surface tensions of the solid-gas, solid-liquid and liquid-gas interface, respectively, and θ is the contact angle. The contact angle provides an easy tool to measure the hydrophobicity of a surface. Contact angles on plates are commonly determined by sessile drop (fig 2.5a) or sessile bubble (fig 2.5b), where the angle of a droplet or a bubble in solution on a polished solid surface is measured through the vapor or liquid phase.

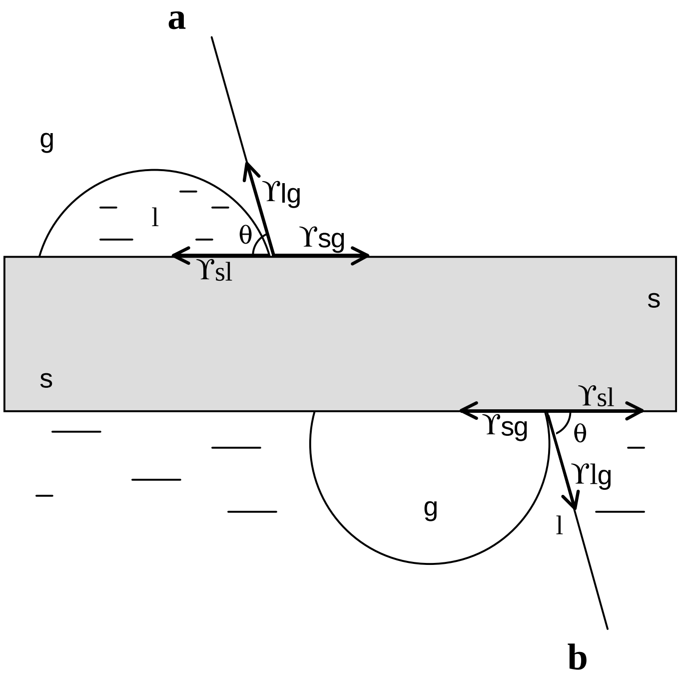


Fig 2.5 *Contact angles by sessile drop (a) or sessile bubble (b)*

In general, the higher the contact angle the higher the hydrophobicity of the surface and the better a bubble will attach to the surface. Therefore, the larger the contact angle the better the flotation recovery.

For particles of a particular size there is a critical contact angle above which flotation is strong (Crawford et al. 1988).

2.3 Fine Particle Flotation

Separation of small particles or fines often cause problems in flotation. In flotatoion, fines are mostly not only colloidal particles but, are defined as all particles below 10 µm (Trahar 1981). Factors like entrapment, entrainment, high specific surface areas and froth stabilization lead to reduction in efficiency and/or selectivity (Trahar 1981; Kirjavainen 1996).

Entrapment problems occur when fine hydrophilic particles (gangue) become physically trapped by hydrophobic particles or bubble-particle aggregates. Problems stemming from entrapment are sometimes reported as relatively minor (Fiscor 1992). However, the general view is that it is a main cause for high gangue recoveries (Kirjavainen 1996).

Hydraulic entrainment occurs when particles are recovered in the liquid film between air bubbles in the froth. Entrainment becomes prominent when large quantities of fine particles are treated (Fiscor 1992). The recovery due to entrainment will increase with water recovery, fine particle size and high slurry density (Johnson et al. 1974; Warren 1984). It has been suggested that the concentration of non-settling gangue in the froth aqueous phase is equal to the concentration of the gangue in the pulp from which the froth is generated (Hemmings 1980; Hemmings 1981). Entrained gangue particles are able to drain back into the pulp via the network of channels formed by the interface bubble water. The coarser particles tend to drain from the froth more rapidly than the fines and there is consequently very little entrainment of siliceous gangue coarser than 30 µm. (Johnson, McKee et al. 1974; Trahar 1981).

Small particles also tend to have large specific areas, which can lead to excessive adsorption of reagents, and other effects associated with chemically active particles (Warren 1984; Feng et al. 1999). Next to that, small particles show slow recovery rates, owing to decreased particle-bubble collision frequency, leading to a low rate of attachment (Trahar et al. 1976; Feng and Aldrich 1999). Furthermore, small hydrophobic particles will have a stabilizing effect on the structure of the froth (Warren 1984; Bayraktar et al. 1998). However at very low concentrations fine hydrophobic particles could destabilize the froth (Kirjavainen 1996).

2.4 Flotation Reagents

2.4.1 Introduction

Reagents used in the froth flotation can be broadly classified into three groups, namely collectors, frothers and regulators (Leja 1982; Lovell 1982; Heerema 1995).

2.4.2 Collector

These are the reagents that render the hydrophobicity to the particles. They are usually surface-active compounds. They comprise a polar functional group, hydrophilic in character, through which they attach to a particle, and a non-polar hydrophobic tail, through which they attach to the bubble. The hydrophobic tail is usually an aliphatic chain. Also non surface-active compounds, like short-chain thiol molecules and oil, can act as collector (Lovell 1982).
Collectors can in turn be divided in to a number of sub-groups based on the functional group involved and on the type of mineral collected (Leja 1982; Lovell 1982; Heerema 1995). According to lovell they are classified into thio-compounds, anionics, cationics and nonionics.

2.4.2.1 Thio-compounds

These are characterized by a functional group that contains a sulfur atom bonded to a carbon or phosphorus atom, but not to oxygen. They are used in the flotation of sulfide minerals.

2.4.2.2 Organics acids and salts – the anionics

These are ionizable, non thio compounds. Their anionic form predominates in flotation pulps (depending on the pH) and they are used to collect a widerange of oxide, silicate and salt type minerals. They are usually strong surface-active and exhibit powerful frothing properties.

2.4.2.3 Organic derivatives of ammonium hydroxide – the cationics

This group is represented by the amines which, below certain pH values, exist in the cationic form. They are used to float sylvite (KCL) from halite (NaCl) solutions and silica from rougher concentrates of phosphate rock.

2.4.2.4 Non polar oils and hydrocarbons

A number of non polar hydrocarbons and oils are used as collectors, either alone for readily or naturally floatable minerals, or together with conventional collectors, to extend the hydrophobic effect of the collector. A wide variety of such materials is available for example, kerosene, naphtha and fuel oils (diesel).

2.4.3 Frothers

Frothers are surface-active molecules whose function in the flotation system is to provide a larger air-water interface of sufficient stability to ensure that a floated particle will not fall back into the flotation pulp before it can be removed. Frothers also have an influence on the kinetics of the attachment of the particle to the bubble. Unlike the collectors it is particularly difficult to associate a certain type of frother with any particular mineral system. The type of froth produced by a certain frother will depent upon the nature of the collector, the type and particle size of the particles in the froth and the presence of other organic and inorganic species in solution, as well as on the type of frother. Mechanical factors, like size and aeration of the flotation cell are also important. The frothers can be divided into several groups (Lovell 1982; Cooper et al. 1985; Hansen et al. 1987). Lovell divided them into alcohols, alkoxy-type, and polyglycol type.

2.4.3.1 Alcohol type

Aliphatic alcohols (ROH), Both straight (C6 to C9) and branched (C6-C16) chain compound are used. These frothers give fine-textured, fairly selective froths that are brittle and therefore do not give problems with entrainment.

Cyclic alcohols, these are represented by the pine and eucalyptus oils. The active frothing constituent are the terpene alcohols.

Aromatic alcohols, The major example of this type finding industrial application is cresylic acid.

2.4.3.2 Alkoxy-type frothers

These frothers a further development from the alcohol type and tend to be somewhat more powerful and selective.

2.4.3.3 Polyglycol – type

They are all low-viscosity liquids that are completely or partially soluble in water and form fine fragile froths that are usually very selective and have no collector action.

2.4.4 Regulators or Modifiers

Frequently in flotation, the collector does not attach adequately to the valuable mineral, or it attaches to the gangue as well. Therefore regulators or modifiers are used, which formally they can be divided into three types (Lovell 1982).

Activators or promoters, Which enhance collector attachment to the valuable mineral.

Depressants, which ensure that minerals other than the valuable mineral do not float by enhancing the hydrophilic character of the gangue.

pH modifiers, which as the name implies, modify the pH of the pulp so that optimum conditions for collection, activation or depression are achieved .

2.5 Coal Flotation

2.5.1 Introduction

The flotation of coal is extensively discussed in this chapter because the flotation of contaminated particles from soil or sediment carried out in this research resembles to some degree to the flotation of coal.

Froth flotation has been used to improve the recovery of fine coal, for minimizing the sulfur and ash content of clean coal and for the removal of fine coal from recycled or discharged backwater from coal preparation plants. It is the only effective and economical means of recovering coal smaller than 0.15 mm on industrial scale. Coal froth flotation technology was derived from its ore flotation “sibling” (Aplan 1999; Meenan 1999). Coal is a solid combustible material that results from the alteration of vegetable matter largely in the absence of air. It is essentially a catch-all term covering a wide range of coal ranks, all with highly variable chemical and physical properties. There is a wide variation in properties as coal progresses in rank from lignite to anthracite. Of especial interest is the great variability in the hydrophobicity, and hence, the floatability of various coals (Aplan 1999).

Lignite is the coal which is the most difficult to float. Subbituminous coals are also highly hydrophilic and therefore, hard to float. With the continuing carbonification (higher rank), the coal becomes easier to float. Medium volatile bituminous coal is suggested to be the easiest to float. Then the trend reverses and anthracite floats more reluctantly (Wheeler et al. 1987; Aplan 1999). Three main factors can be claimed to be mainly responsible for the surface properties of coal particles: Hydrocarbon skeleton (related to rank), oxygen functional groups and inorganic impurities (Laskowski et al. 1984).

Oxidation alters both physical and chemical properties of the surface of the coal particles. The coal disintegrates, more colloidal fines are created; the surface of the coal has microfractures; aromatic, high-boiling, benzene-soluble oils are washed away from the surface and the oxygen content increases. All these phenomena results in lower floatability of the coal. The first indication that oxidized coal is being processed is a drop in the slurry pH (Laskowski and Miller 1984; Wheeler and Keys 1987).

The coal flotation process requires not only the recovery of valuable constituent, but also the rejection of the worthless. The presence of clay together with the humic acid created during oxidation are the main culprits for the flotation efficiency and often desliming can help. Kaolinite and illite clays are not significant flotation poisons. Bentonite clays substantially reduce the coal recovery (Arnold et al. 1986).

Already in a early stage researcher found that the optimal coal recovery finds place at a pH of around 7 (Stewart 1932; Chang 1947; Zimmerman 1948) in (Aplan 1999) and (Firth 1999). Nowadays most plants still run at a pH of 7 (Aplan 1999).

2.5.2 Reagents in Coal Flotation

Frothers have by far the largest effect on the amount of coal recovered. In coal flotation the frothers not only act as bubblemaker but they also serve in a seldom acknowledged role of collector (Wheeler 1995).

Higher ranks coals that have higher natural floatability need only a frother to float. Usually an aliphatic alcohol frother is most successful (Wheeler and Keys 1987; Wheeler 1995). Methyl Isobutyl Carbinol (MIBC) was the most popular frother in 1980. Other alcoholic frothers like the Aerofroths are also popular (Aplan et al. 1987).

Typical MIBC dosages in Australian flotation circuits are about 10 g/ton of water which is in photographic evidence with the work of Eveson (Eveson et al. 1957; Firth 1999). Aplan suggested on average of 0.25 lb frother/ton of coal is used (Aplan, Chandler et al. 1987).

Traditionally neutral hydrocarbon oils are the principle collectors in coal flotation (Wheeler and Keys 1987). For Australian coal the hydrocarbon oil, Diesel, is the preferred collector (Firth 1999). Collectors are often added at the same place and at the same time as the as the frother. In many cases it will be desirable to add the collector to the system in an earlier stage than the frother, to facilitate the adequate dispersion of the insoluble oily collector. Alternatively, they may be pre-dispersed as an oil-water detergent emulsion prior to their use (Aplan, Chandler et al. 1987). The efficiency of the hydrocarbon oil collector can be increased by the emulsification and higher recoveries can be achieved (Laskowski and Miller 1984; Wheeler and Keys 1987). The water-in-oil emulsions will disperse more readily than neat hydrocarbon oils. The stability of the emulsions is increased when frothers were added to the oil collectors prior to the emulsification (Wheeler and Keys 1987). For readily floatable coal dosed of <1 lb/ton of oil is used (=<0.5 kg/metric ton). Lower rank and oxidized coals require progressively more oily collector (Aplan, Chandler et al. 1987; Arnold 1999). When dealing with oxidized coal, sulfhydryl compounds including dialkyldithiophosphates are suggested to be good activators for them, when clays are present (Jowett 1983).

A collector is not usable when it gives a certain hydrophobicity to the particles at which they agglomerate and settle. However, in coal flotation agglomeration or flocculation can facilitate the flotation and if particles do not settle, it can be useful to have a strong collector (Osborne 1988; Song et al. 1999)

As mentioned before, the flotation of lower rank or oxidized coal, i.e. more hydrophilic coals, is more difficult than the flotation of higher rank coals. In the past the solution was to swamp the circuit with additional fuel oil hoping that some of it would attach to the coal (Townsend 1982). Modern technology offers help in the form of conditioning reagents, like promoters and emulsifying agents which have a positive effect on coal flotation. The role of each is confused by the fact that some promoters have the ability to act as dispersants and some emulsifiers are collectors, and they can act as promoters. Basically, the emulsifiers act as the vehicle to deliver the collector to the coal particle, where the promoters take over and provide a more secure bubble-particle attachment (Wheeler and Keys 1987).
A possible mechanism of the influence of an alcoholic or ionic promotor on the attachment of oil droplets on coal surfaces is given is presented in fig 2.6. (Melik-Gaykazian et al. 1967; Mackenzie 1970; Wheeler and Keys 1987).

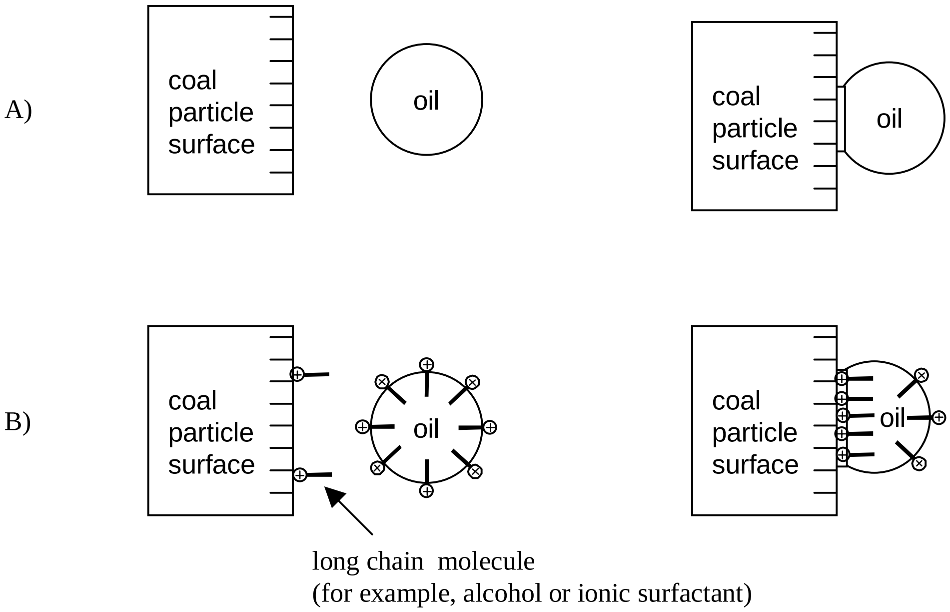


Fig 2.6 *Attachment of a oil droplet on a coal particle with (B) and without (A) the aid of a promotor (after Mackenzie 1970; Melik-Gaykazian 1967; Wheeler 1987)*

2.6 Flotation Equipment

2.6.1 Introduction

Flotation cell designs are mostly based on pragmatism and there exists no rational way to make the best selection of plant, for every new froth flotation installation. The difference between the best and worst choices can be very large, particularly for flotation processes dealing with unusually fine or coarse materials (Young 1982; Barbery 1984). Flotation systems can be divided into four classes, Mechanical, Pneumatic, Disoolved Air and Electro (Heerema 1995).

2.6.2 Mechanical Flotation

This is the oldest type of flotation cells and the bubbles are created by mechanical stirring. They can be divided into agitating (mixing by blades) and sub-aerating cells (mixing by impellers). Industrially, the sub-aerating cells, are still the most important and most frequently used type of flotation machines (Heerema 1995). The size of the air bubbles is mostly larger than 1 mm (Zabel 1984).

2.6.3 Pneumatic Flotation

With pneumatic cells the air is induced under pressure, eventually together with the pulp or water. The distribution of bubbles is obtained by spreading of the air injection points or infiltration by porous beds (Heerema 1995).

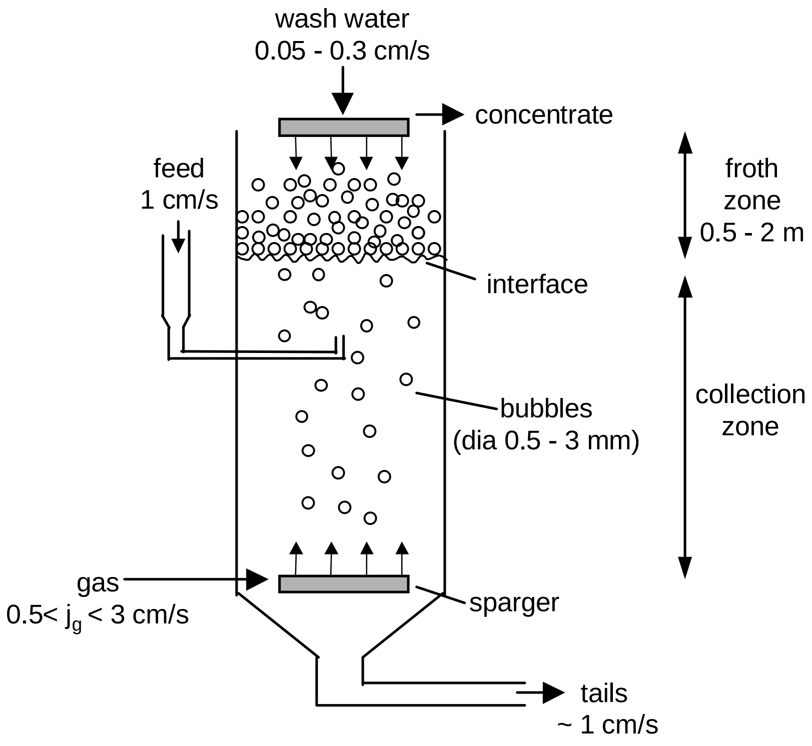


***Fig 2.7** Column flotation cell (after Finch 1995)*

An example of a pneumatic flotation system is the Column flotation cell. A schematic drawing of the design of flotation columns is given in figure (2.7). Three characteristic features are the use of a sparger to generate bubbles, a counter-current slurry/bubble flow in the collection zone, and a deep froth zone (0.5-2m) coupled with the use of wash water to induce a “cleaning action” (Finch et al. 1995). The design is known in Canada since the in the early 60’s. The column flotation will have a higher selectivity than conventional cells and is therefore mostly used in the cleaner stage (Heerema 1995).

A variation on the column flotation cell is the Jameson cell (figure 2.8). The Jameson cell is a type of flotation column in which the air and pulp are brought together in a vertical tube called the downcomer (Jameson 1988; Evans et al. 1995; Honaker et al. 1999). Typical bubble sizes in the Jameson cell are 300-600 μm (Evans, Attkinson et al. 1995).

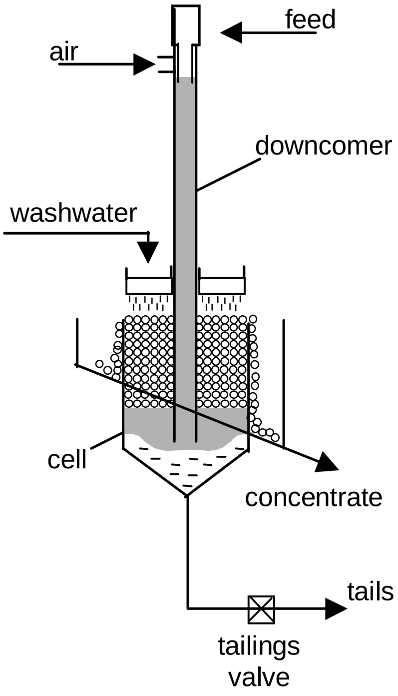


Fig 2.8 *Jameson flotation cell (after Honaker 1999)*

Another variation on the column flotation cell is the Rubio cell. In the Rubio cell drained particles are selectively separated from the froth zone resulting in a third product. Also a secondary wash water system between the feed and froth zone is used.

A very special flotation system is the flotation in a centrifugal force field. The centrifugal force can be induced by a flotation cyclone, a air sparged hydrocyclone or a flotation centrifuge. The process is a promising tool to float fine particles (Tills 1990; Niewiadomski et al. 1999).

2.6.4 Dissolved Air Flotation (DA Flotation)

DA flotation uses bubbles of air generated under controlled conditions by pressure release, from a super-saturated solution of air in water (Gallios et al. 1995). To obtain small bubbles, water is mostly released through a nozzle. The size of the microbubbles is therefore depending on the geometrical design and operating conditions of the injection nozzles (Rykaart et al. 1995; Dupre et al. 1998; Ponasse et al. 1998). Some typical air injection nozzles are presented in figure 2.9.

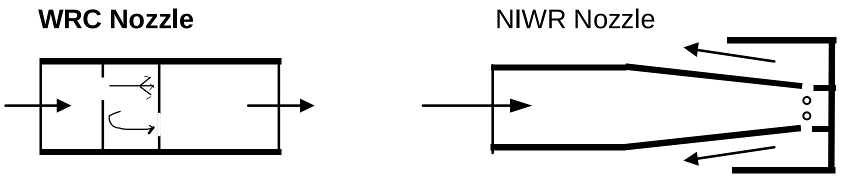


Fig 2.9 *Typical injection nozzles (after Rykaart 1995)*

Generally, The micro-bubbles formed by DAF have a diameter between 10 and 120 µm and a reasonable estimation of the average bubble diameter is 40 µm (Edzwald 1995). Additional bubble growth may occur as the bubbles rise in the flotation tank due to a decrease in the hydrostatic pressure or by coalescence. Both of these have negligible effects on the small bubbles formed in DA systems, but the coalescence of bubbles on the walls of hydrophobic tubes do lead to the formation of macro-bubbles (Edzwald 1995; Ponasse, Dupre et al. 1998). The formation of these bubbles greater than 500 µm, seems to be linked with the DA flotation process and is often observed by the users of dissolved air flotation (Dupre, Ponasse et al. 1998). DA flotation cells are mainly used in the field of wastewater treatment (Haarhoff et al. 1993; Edzwald 1995). A picture of a DA flotation unit is presented in figure 2.10

2.6.5 Electro Flotation

The basis of electrolytic flotation is the generation of hydrogen and oxygen in a dilute aqueous solution by passing a direct current between two electrodes. The bubble size generated in electrolyte flotation (2-100 µm) is generally smaller than that in dispersed and dissolved air flotation. For small water treatment installations, in the flow range of 10 to 20 m3/h, electro flotation has found to be a versatile and competitive system. For larger plants DA is more economical (Zabel 1984; Heerema 1995).

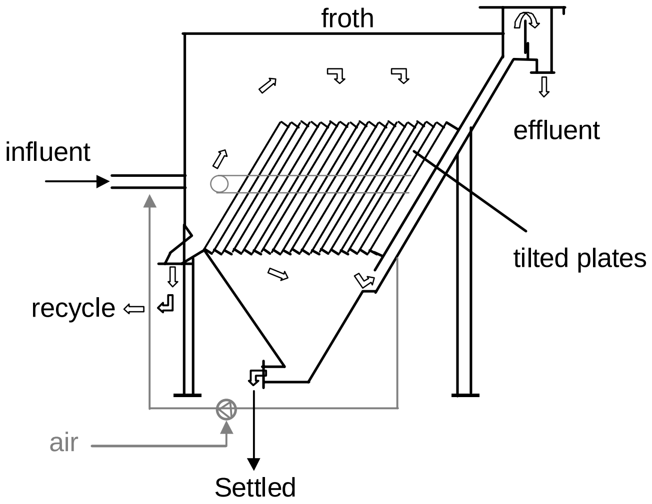


Fig 2.10 *A DA flotation cell (after Nijhuis Water Technolgy, NL)*

2.7 Flotation in relation to soil remediation

Flotation plays and important role in the soil washing process were it is used as one of the classification techniques (see chapter 1.4.1). Often flotation is used for further treatment of the sand fraction or to remove the slimy particles from the process water (Wilichowski 1995; Hoek et al. 2001). But flotation can also be used as the only remediation process involved to clean contaminated soil or sediment. Several researchers have investigated the possibilities of the use of the flotation technique for the remediation of contaminated soil or sediment.

Cauwenberg (Cauwenberg et al. 1997; Cauwenberg 1998; Cauwenberg et al. 1998; Cauwenberg et al. 1998) studied the flotation of heavy metal contaminated dredged sediment, using a Denver cell. It is found that specific collectors (xanthate, dithiophosphates) did not result in a better yield than non specific oily collectors because of the large amounts of fine material plus high amount of organic matter in their sludge. Best results were obtained with kerosene and 80 to 85% of the metals were concentrated in 30% of the mass. The 20-50 µm fraction showed the best results. For the smallest fraction however, considerably lower results were obtained and it is suggested that a specific reactor could help to improve flotation efficiency of smallest fraction. Flotation did not further enhance selective separation of some cycloned soil fractions. Next to that, the flotation on different sediments showed that flotation was only successful for some sediments.

Other studies on the remediation of a heavy metal contaminated soil are performed by Langen (Langen et al. 1994) and Seselj (Seselj et al. 1997). Seselj used column flotation to remediate zinc and lead contaminated soil. The recoveries for zinc (70%) and lead (91%) were high but mass and metal concentration of reusable tailings are not mentioned. Venghaus and Werther (Venghaus et al. 1998) also performed a study on a zinc contaminated soil. They found that flotation reagents commonly in use in the processing of fine ores can also be used for the clean up of heavy metal contaminated soil. The underflow of a hydrocyclone (40-355 µm) was treated with additional flotation which improved the soil washing process significantly. Wilichowski (Wilichowski 1994; Wilichowski 1995; Wilichowski et al. 1998) showed that flotation also can further clean a hydrocyclone fraction (40-355 µm) of a mineral oil contaminated soil.

Some other researcher also investigated the possibility of the remediation of oil contaminated soil by flotation. Chou (Chou et al. 1998) removed paraffin oil from spiked soils using column flotation. Up to 80% of the contaminant was removed from the coarse fraction (250-800 um) the total fraction (75-800 µm) showed removal efficiencies up to 65%. The removal efficiency by flotation was higher than those obtained by soil washing. In other related research of bench scale flotation of soil, artificially contaminated with paraffin oil in a Denver cell. Sodium dodecylsulfate was used ad frother. For soil particles in the range of 75-83 µm the removal was 58%. Preliminary attrition enhance oil removal by 10% and another 5% was removed using a two-stage flotation (Somasundaran et al. 2001; Zhang et al. 2001).

Clifford (Clifford 1993) also removed oil from river sediment. He used conventional flotation methods and triton and Igepal CO as flotation agent. Best results showed that 76% of the oil and also grease was concentrated in 13.5% of the mass.

Pearl (Pearl 1995; Pearl et al. 1996) performed two investigations to the potential techniques to overcome limitations created by fine particles during ex-situ soil washing. Flotation was the best potential techniques to treat the fines of a gasworks soil. A three stages rougher cleaner scavenger flotation circuit showed reductions of PAH by 61%, petroleum hydrocarbon by 54% and cyanide contamination by 39%. The resulting contaminated reduced non floating fraction was 69% by weight of the original 10-63 µm fraction. However, significant contamination remaining in the “treated” product made it unlikely to be suitable for reuse.

Bilz (Bilz et al. 1994) guided by mosmans mineraal techniek, floated the finest fraction of a heavy metal and PAH contaminated sediment. He suggested good recovery but there is a poor explanation of obtained results.

Kasi used coal as a cleaning agent to strip off the contaminants from the soil whereafter it was separated by a process called agloflotation (Kasi et al. 1993). The coal agloflotation cleaned a PAH contaminated soil up to 95%.

Also research has been done on the combination of flotation and microbial degradation. The combination of the two remediation techniques leaded to a much higher reduction than separate techniques, especially for 3 till 6 ring PAH. (Klein et al. 1995). Another study were flotation and bioremediation are combined is performed by Uhlberg (Ulberg 1997).

Eberius and Ekke (Eberius et al. 1989) patented their experience on the removal of heavy metals from sediment by flotation. Another patent to remediate the coarse fraction of a hydrocarbon contaminated soil by flotation is made by Varadaraj (Varadaraj 1994).

3

Flotation of Soot Particles from a Sandy Soil Sludge

Abstract In this study the froth flotation technique was applied to clean a sandy soil sludge contaminated with soot particles containing a large amount of polycyclic aromatic hydrocarbons (PAH). To obtain insight into the flotation process, contact angles on soot pellets and silica plates were determined in both the absence and presence of several collectors and the results were compared with the flotation recovery of soot (90-200 µm) and silica (90-200 µm) from suspensions of the pure materials using a modified Hallimond tube. Aerophine, dodecylpyridinium chloride and three different oils were used as collectors. Adding a collector increased the contact angles on soot particles from 89° to at least 100° and increased the flotation recovery from 56% to 100%. However, the contact angle and the flotation recovery of silica are also enhanced under optimal conditions for soot flotation.

A semi-continuous dissolved air flotation apparatus was used for the practical flotation experiments. The contaminated sludge fraction contained silica particles of 20 to 125 µm and soot particles of 20 to 500 µm. The best flotation results were obtained when a combination of emulsified diesel oil as collector and emulsified Montanol (a mixture of higher alcohols) as frother was used. Under optimal conditions 95% of the PAH were removed and concentrated in only 2.5% of the total mass of the sludge.

Mulleneers, H.A.E., Koopal, L.K., Swinkels, G.C.C., Bruning, H., Rulkens, W.H. (1999). Colloids and Surfaces A, 151: 293-301

3.1 Introduction

Ex-situ physical classification of contaminated soil is a widely used method to remediate polluted soils. Usually the process is a separation of clean and contaminated soil fractions based on differences in particle size and density of the two fractions. This kind of treatment has proven to be very successful, especially for sandy soils with particles above 90 µm. The process turned out to be less successful when a large fraction of soil particles below 63 µm in size is present (Werther et al. 1990; Feenstra et al. 1995; Rulkens et al. 1995). The classification technique is also not suitable when the polluted and clean particles hardly differ in density or size. This is the case when the pollution is only present at the surface of the soil particles or when the density of the contaminating particles is similar to density of the soil particles. In cases were the classification techniques fail, flotation techniques have proven to be a successful alternative remediation technique (Clifford 1993; Bilz et al. 1994; Wevers et al. 1995; Wilichowski 1995).

Flotation techniques are far from new and have been used in applied mineralogy for almost 100 years (Kitchener 1984). A parameter describing the success of the flotation process is the flotation probability or collection efficiency, which is given by the product of the collision efficiency, the attachment efficiency of particles and bubbles and the stability efficiency of the bubble particle aggregate (Derjaguin et al. 1961). The particle-bubble collision efficiency mainly depends on the density of the slurry, the size of both the bubbles and the particles and on the hydrodynamics in the reactor (Schulze 1984; Schulze 1993). A collision between bubble and particle does not necessarily result in attachment. For attachment an “induction time” is needed to drain away the thin liquid layer between the particle and the bubble to permit coalescence to occur (Jameson 1984). In the attachment process the solid, liquid and gas phases meet each other at the line of contact between the three phases, and a dynamic contact angle is established (Ralston et al. 1992). The magnitude of the contact angle is an important parameter for the attachment efficiency and therefore for the flotation efficiency itself (Crawford et al. 1988; Subrahmanyam et al. 1996). Although in the flotation process the dynamic contact angle is relevant, many experiments (Fuerstenau 1957; Fuerstenau et al. 1964; Fuerstenau et al. 1972; Koopal et al. 1999) have shown that there is also a strong correlation between the flotation efficiency and the magnitude of static contact angle. The larger the contact angle, the better the flotation recovery is. When attachment has been realised the stability efficiency of the particle-bubble-aggregate determines whether or not the aggregate reaches the “foam layer”. To enhance either or both the collision efficiency and the attachment efficiency and thereby the flotation efficiency, in general a “collector” is added that modifies the surface properties of particle and bubble. To enhance the stability efficiency “frothers” that produce a stable foam can be added (Leja 1982; Jones et al. 1984; Crozier et al. 1989).

In this paper we focus on the remediation of a sandy soil sludge contaminated with soot particles by dissolved air froth flotation. To investigate the behaviour of the system, the effect of three different types of collectors on the static contact angles on both silica plates and soot particles is compared with the flotation recovery of soot or silica from suspensions of the pure materials. To screen the ability of the collectors in a more practical situation, some batch flotation studies are carried out using the polluted sludge fraction. Finally, the polluted sludge is treated in a semi-continuous flotation approach, to investigate the optimal flotation conditions.

3.2 Experimental

3.2.1 Materials

3.2.1.1 Reagents

Inorganic chemicals used with the experiments are of analytical grade. Water is demineralized using a mixed bed ion exchanger. However, tap water is used for the original sludge. The hardness of the tap water based on the total Mg^{2+} and Ca^{2+} concentration is 0.79 mmol/l. Dodecylpyridinium chloride (DPC), n-hexadecane and sodium dodecylsulfate (SDS) are obtained from Aldrich. DPC and n-hexadecane are used as collector, SDS is used as frother. Aerophine 3418a, a commercial collector, is a 50% aqueous solution of sodium di-isobutyldithiophosphinate and Aerofroth 76a, a commercial frother, is a mixture of C4-C7 alcohols. Aerophine and Aerofroth are obtained from Cytec Industries B.V. (The Netherlands). The other frothers; Montanol 350, a technical mixture of mainly higher alcohols and esters with additives and Flotanol C7, a technical grade alkyl polyethylene glycol, are obtained from Hoechst A.G. (Germany). “Diesel” is a technical grade oil composed mixture of C15-C25 alkane chains with additives. “Biodiesel” is a technical grade natural oil with a high content of glycerine and methylesters of fatty acids.

Emulsions of Diesel and Montanol are obtained by intensively blending 1 ml Diesel or 1 ml Montanol in 99 ml water with 1 ml of a 0.1 g/l Eumulgin ET 10 solution. Eumulgin ET 10 is a commercial ethoxylated fatty alcohol obtained from Henkel A.G. (Germany). These emulsions can be easily dispersed in water and they are used in the practical flotation tests.

3.2.1.2 Sludge

The sludge from the contaminated site consists predominately of silica and soot particles. The soot particles, the result of the incomplete combustion of cables and tires ended up in the soil by deposition. The sludge fraction used for this study is obtained by classification and contains silica particles in the range of 20-125 µm and soot particles in the range of 20-500 µm. The sludge fraction is selected because the soot particles, despite having a lower density of silica, could not be removed from the sludge by the classification process. Approximately 97.5 % (m/m) of the sludge is silica, and the other 2.5 % is mainly soot. The presence of soot particles pollutes the soil with polycyclic aromatic hydrocarbons (PAH). The concentration of PAH in the sludge is 25.6 mg/kg d.m.

3.2.1.3 Soot sample

A soot sample is obtained from the contaminated sludge by collecting the sieved fraction between 90 and 200 µm. From this fraction the sootparticles are isolated by batchwise flotation in a modified Hallimond tube (see fig. 3.1) with Aerophine as collector. The sludge (17.5 g d.m.) is conditioned in the Hallimond cell for 15 minutes using 0.25 ml Aerophine in 100 ml water before the flotation is started. The particles carried with the foam are collected and repeatedly washed with demineralized water to remove the Aerophine. This sample is called Soot-F. To measure the contact angle of the Soot-F samples, the soot particles are pressed into pellets at 13000 kg/m^2.

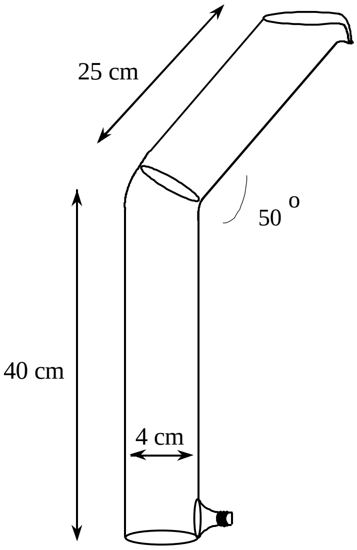


Figure 3.1 Modified Hallimond tube

3.2.1.4 Silica samples

Flotation tests with pure silica are carried out with a sample containing particles of 40 to 125 µm, acquired. The sample is obtained by mixing two samples of Merck Kieselgel 60 (40-63 µm and 63-125 µm) in a 1:1 ratio. It is not possible to press the silica particles into stable pellets. Therefore, oxidised silicon wafers from Wacker Chemitronic (Germany) are used for the contact angle experiments. The wafers of the Czochralsky-type are oxidised in an oven at 1000^{o} C for 1 hour to produce a silica layer of about 100 nm. After oxidation the wafers are cut into strips that are cleaned by a UV-ozone treatment and used immediately after the cleaning step. In another study a good correlation has been found between stability, contact angles and flotation of different silica-samples in presence of DPC (Koopal, Golub et al. 1999).

3.2.2 Methods

3.2.2.1 Contact Angles

The contact angles are determined on sessile drops using a contact angle microscope with goniometer (Erma Contact Angle Meter G-1). The contact angle is measured on the oxidised silicon wafer strips and on soot-pellets. Aerophine and DPC solutions of varying concentrations and saturated solutions of the oils all in 0.01 M NaCl and pH=6 are used as wetting agents.

3.2.2.2 Batch flotation of silica or Soot-F

The flotation behaviour of individual Soot-F and Kieselgel (40-125 µm) particles are tested separately. The modified Hallimond cell (see fig. 3.1) is totally filled, with a 0.01 M NaCl solution of pH=6 and a certain concentration of Aerophine or DPC, or with a 0.01 M NaCl solution saturated with one of the oil-type collectors. One gram of dry particles is added to the solution and the suspension is conditioned by stirring it for 15 minutes. Then from a vessel, pressurised at 7 bar, an air saturated water solution of the same composition as the conditioning solution is fed (100 ml/min) into the cell and the flotation is carried out for 10 minutes. The floated material is collected in a Büchner funnel and dried at 60^{o} C to establish the flotation recovery.

3.2.2.3 Batch flotation screening tests

To screen combinations of collector and frother on their ability to separate the soot particles from the contaminated sludge, flotation tests are performed batchwise in the modified Hallimond tube. In this case the Hallimond tube is filled up to 5 cm with water and 25 grams of wet sludge (approximately 17.5 g d.m.). The collector is added to this suspension and the sample is conditioned by stirring. After 3 minutes the frother is added and the suspension is conditioned again for 3 minutes. Pressurised water saturated by air is then fed into the cell (80 ml/min). When the water has reached the bend in the flotation tube, 1 ml of a 2 mol/l SDS solution is added along wall to the foam at the top of the cell to further increase the stability of the froth. The test is stopped when the tube is totally filled and the froth can be removed from the top of the cell. Aerophine, Diesel and DCP are tested as collectors in different concentration ranges. Aerophine is tested together with different concentrations of Aerofroth. Diesel is tested together with Montanol and/or Flotanol. In this series also tests with emulsified Diesel (e-Diesel) plus emulsified Montanol (e-Montanol) are performed. The efficiency of the sludge flotation in these screening tests is judged visually on the amount of soot particles in the froth and the tailing.

3.2.2.4 Semi-continuous sludge flotation

The semi-continuous dissolved air flotation experiments with the contaminated sludge fraction are carried out in a specially build flotation apparatus with a tilted tube behind the mixing zone to increase the separation efficiency. The equipment is shown schematically in fig. 3.2.

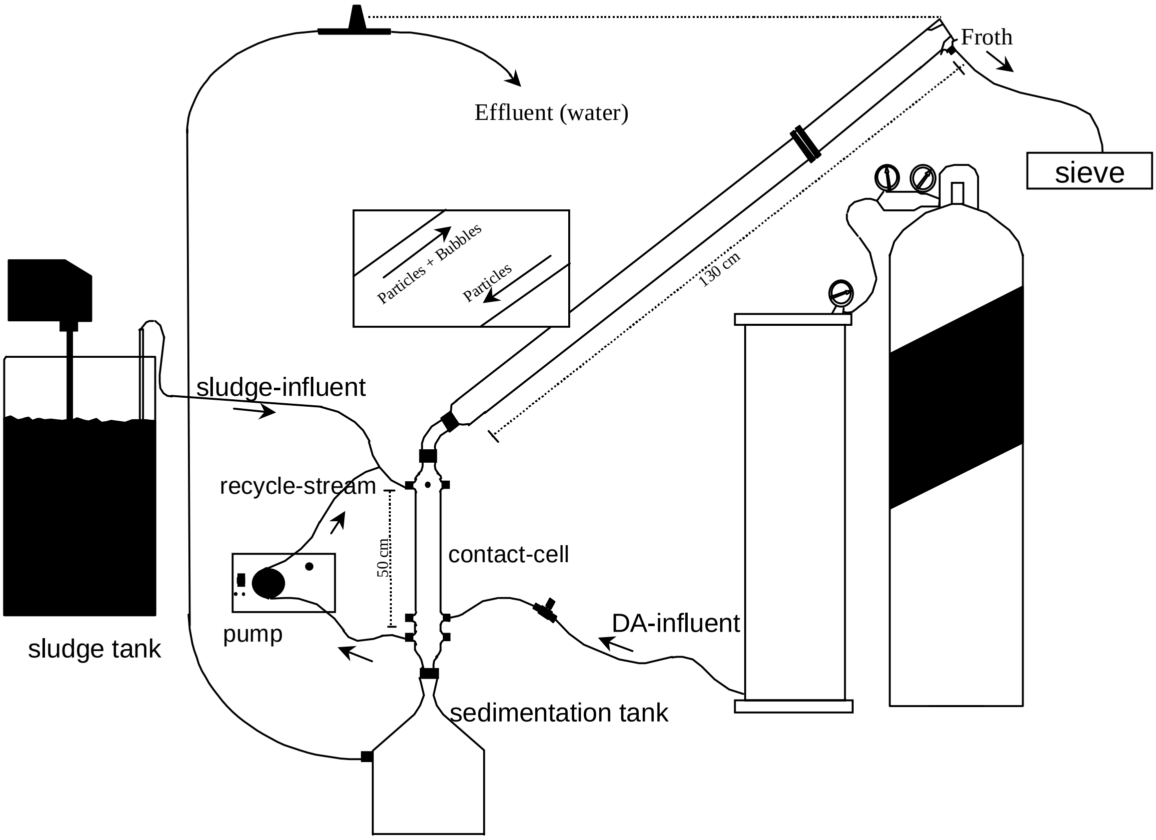


Figure 3.2 Schematic drawing of the semi-continuous flotation equipment.

It is composed of a sludge tank, a sedimentation tank, a mixing compartment where the sludge stream and the water stream with dissolved air meet and a tilted tube where particles attached to bubbles float to the froth and the bare particles sink to the mixing compartment. Sludge in 2 liter slurries (25% (m/m)) was conditioned with different combinations of reagents: e-Diesel, e-Diesel plus eMontanol, e-Diesel plus Flotanol, and e-Diesel plus e-Montanol plus Flotanol. The e-Diesel and e-Montanol were added in a 30 ml emulsified solutions (which means 0.3 ml of pure Diesel and Montanol) per 100 g dry sludge and also Flotanol was added with 0.3 ml per 100 g dry sludge. After conditioning the sludge for 20 minutes, the slurry is diluted to 5% (m/m) and fed into the mixing compartment, with a flow rate of 60 ml/min. Simultaneously the flow of water with dissolved air is started at a rate of 100 ml/min. Similarly as with the batch flotation tests, aliquots of SDS were added at the top of the tilted tube to increase the stability of the froth. The floated particles are caught in a 20 µm sieve and the non-floated particles in the sedimentation tank.

3.2.2.5 PAH analyses

The samples are dried (60^{o} C) and extracted with a 80% acetone/water solution. The concentrations of 16 PAH selected by the Environmental Protection Agency (USA) (16 EPA-PAH) are determined in the sample extracts. The separation of the 16 EPA-PAH is achieved by using a HPLC column with a length of 250 mm and a diameter of 4.6 mm, filled with Vydac 5, a C18 reversed phase matrix, and eluted with a mixture of acetonitrile and degassed water (flow rate : 1.0 ml/min). The composition of the mobile phase is changed during elution: first a 50/50% (v/v) mixture of acetonitrile concentration and water for 5 minutes subsequently, the acetonitrile is linearly increased to 99% in 15 minutes, after which the acetonitrile concentration is kept at 99% acetonitrile for 19 minutes. The 16 EPA-PAH are measured with a photodiode-array detector and identified in the chromatograms by manual comparison of the sample spectra with that of the 16 standard EPA-PAH.

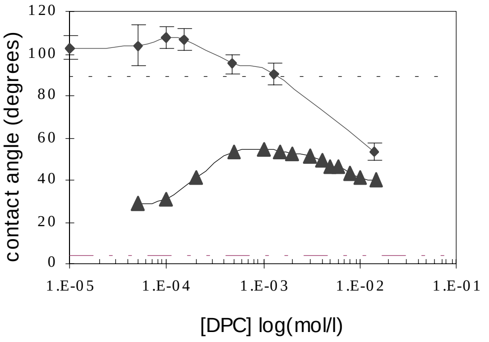
3.3 Results & Discussion

3.3.1 Contact Angles and Flotation of Pure Silica and Soot-F Particles

The results of the contact angle measurements are shown in figs. 3.3, 3.5 and 3.7, and those of the flotation experiments in figs. 3.4, 3.6 and 3.8. The soot-pellets appeared to be slightly porous but the contact angle could still be measured on the pellets. The contact angles with the blank solutions are 89^{o} for the Soot-F sample and 4^{o} for silica plates. In qualitative agreement with these results the flotation recoveries without collector are 56% for the Soot-F particles (90-200 µm) and 4% for the Kieselgel (40-125 µm) particles. These results are presented by dashed lines in figs. 3-8.

3.3.1.1 DPC

Contact angles of 0.01 M NaCl solutions with different DPC concentrations on the silica plates and the soot pellets are shown in fig. 3.3.



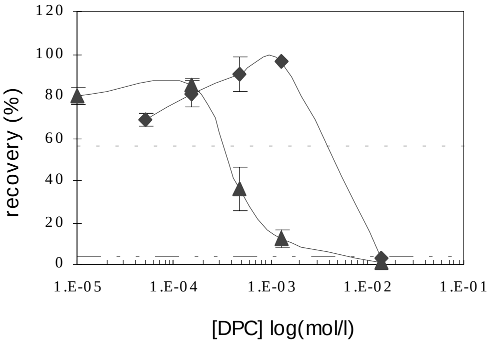


Figure 3.3 *Contact angles of 0.01M NaCl solutions (pH=6) on silica (▲) and soot pellets (◆), as function of DPC concentration (mol/l). In the absence of DPC, the contact angle on silica and soot are 4° and 89° respectively, these values are indicated by dashed lines.*

Figure 3.4 *Flotation recovery of 0.01M NaCl solutions (pH=6) on silica (▲) and soot pellets (◆), as function of DPC concentration (mol/l). In the absence of DPC, the recovery of silica is 4% and that of soot is 56%, these values are indicated by dashed lines.*

The contact angle on silica in presence of DPC first increases from 29° at 0.5 x 10^{-4} mol/l DPC to 54° at 1 x 10^{-3} mol/l DPC after which it decreases to 40° at the critical micelle concentration (CMC) of 1.4 x 10^{-2} mol/l DPC. The lowest DPC concentration tested, already raises the contact angle of soot pellets to 103° and the contact angle stays high up to a DPC concentration of about 2 x 10^{-4} mol/l. For concentrations larger than 2 x 10^{-4} mol/l the contact angle on the soot pellets decreases to 53° at the CMC.

Small concentrations of 1 x 10^{-5} mol/l DPC already increase the recovery of the silica particles up to 85% (see fig. 3.4). Above a concentration of about 1 x 10^{-4} mol/l DPC the recovery rapidly decreases to zero at the CMC. The strong decrease in contact angle and flotation is due to the formation of a surfactant bilayer at the silica surface (see also ref. Koopal, 1999).

The enhancement of the flotation of soot particles in the presence of DPC increases slowly with increasing DPC concentration to a concentration of about 1 x 10^{-3} mol/l, thereby raising the recovery to 96%. For concentrations larger than 1 x 10^{-3} the soot particle recovery decreases strongly. The initial slow increase in the soot flotation recovery does not directly correspond to the contact angle behaviour. A high contact angle of about 100° is obtained even at very low DPC concentrations. The strong decrease in flotation recovery at DPC concentrations larger than 1 x 10^{-3} mol/l correlates well with the strong decrease in contact angle at these concentrations. An important reason for this decrease is that the surfactant molecules adsorb with their aliphatic tails at the soot surface and their head groups directed towards the solution.

3.3.1.2. Aerophine

The presence of Aerophine hardly changes the contact angle on silica (see fig. 3.5).

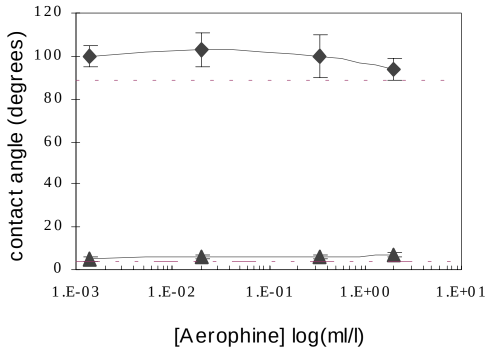


Figure 3.5 *Contact angles of 0.01M NaCl solutions (pH=6) on silica (▲) and soot pellets (◆), as function of Aerophine concentration (ml/l). The contact angles in the absence of Aerophine are indicated by dashed lines.*

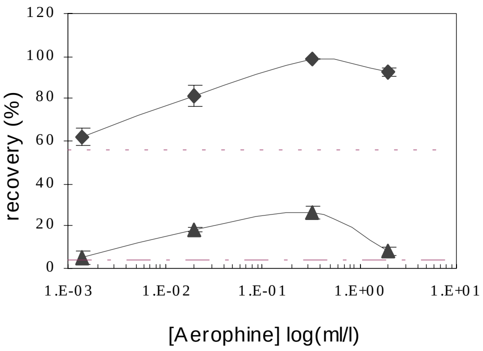


Figure 3.6 *Flotation recovery of 0.01M NaCl solutions (pH=6) on silica (▲) and soot pellets (◆), as function of Aerophine concentration (ml/l). The recoveries in the absence of Aerophine are indicated by dashed lines.*

The contact angles on the soot pellets increase only slightly with an Aerophine concentration of 10^{-3} ml/l and they remain approximately the same over the concentration range studied. Aerophine enhances the recovery of both the soot particles and the silica particles up to a concentration of 0.33 ml/l (see fig. 3.6). The recovery of the silica particles increases gradually to 26% at 0.33 ml/l and then falls back to 8%. The recovery of Soot-F follows a similar pattern and reaches a maximum of 99%. Despite the fact that the contact angle on soot particles is hardly changed by the presence of Aerophine, the recovery is strongly increased. The increased recovery of the silica particles in the Aerophine concentration range up to 0.33 ml/l is also somewhat surprising since the contact angles only increases by 1° or 2°. In this case the lack of correlation might be due to the fact that the silica samples used for both the measurements are not identical.

3.3.1.2 Oils

The effect of saturated solutions of Diesel and Biodiesel on the contact angle on silica is small, and an average increase of 10° is observed. The saturated solutions of the oils have also a small effect on the contact angle of the soot pellets, only the angle with n-hexadecane is about 10° higher (see fig. 3.7).

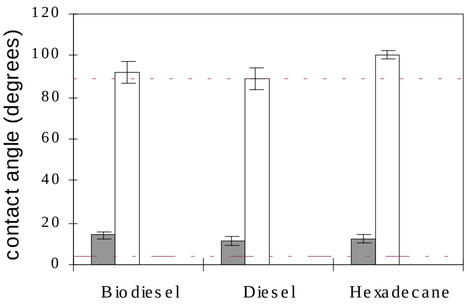


Figure 3.7 *Contact angles of 0.01M NaCl solutions (pH=6) on silica (▮) and soot pellets (□), as function of saturated solutions of Diesel, Biodiesel and n-hexadecane. The contact angles in the absence of the oils are indicated by dashed lines.*

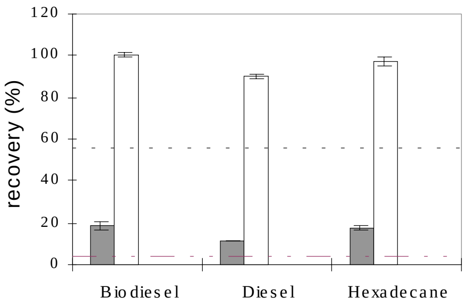


Figure 3.8 *Flotation recovery of 0.01M NaCl solutions (pH=6) on silica (▮) and soot pellets (□), as function of saturated solutions Diesel, Biodiesel and n-hexadecane. The recoveries in the absence of the oil are indicated by dashed lines.*

Saturated solutions of the different oils increase the recovery of silica only slightly, at most to 18 % (see fig 3.8). This small increase in the flotation recovery is expected from the slight increase in contact angles. The recovery of the Soot-F particles is substantially increased to 100% by Biodiesel, to 90% by Diesel and to 98% by n-hexadecane. Based on the contact angles, only a slight increase in flotation recovery of soot particles was expected. The significant increase in flotation recovery might therefore be due to partial coagulation of the soot particles during the conditioning step. The consequence is that the conditioning procedure will be of special importance for the final result if the oils are used as flotation agents.

3.3.2 Screening Tests

The flotation recovery of the complete sludge is strongly dependent on the DPC concentration, as would be expected on the basis of the results shown in fig. 3.4. At DPC concentrations below 1 x 10^{-4} mol/l the flotation result is poor, because of the small amount of floated particles and the non-selectivity of the process. In the DPC concentration range of

2×10^{-4} to 4×10^{-4} mol/l the sludge becomes flocky and all sludge particles float to the surface.

Diesel shows good results when Montanol and Flotanol are added. Apart from floated soot particles, the foam layer with Diesel carried a black liquid of partly dissolved soot particles in the centre and a yellow ring of poorly dissolved Montanol on the edges of the foam. The flotation efficiency in the Diesel experiment could be further enhanced by emulsifying both the Diesel and the Montanol. Some other commercial anionic surfactants (Dowfax 8380, Dowfax 322 and Sykanol) are also screened in combination with Diesel. The tests show that the performance of these combinations is less than that of Diesel combined with Montanol and Flotanol.

Aerophine shows the best results with Aerofroth as frother. At first, the foam layer in the Aerophine experiment carried more soot particles than that in the Diesel experiment. However, after a while the soot particles in the presence of Diesel coagulate and the aggregates float to the foam layer. This makes the final efficiency of the test with Diesel plus Montanol and Flotanol higher than that of the Aerophine with Aerofroth.

The screening tests show that combinations of Aerophine plus Aerofroth and of Diesel plus Montanol and Flotanol are good collecting agents for the selective separation of soot particles from the sludge by flotation, and that with DPC it is difficult to reach a high selectivity. Because the Diesel combination (especially emulsified) is a slightly more successful flotation agent than the Aerophine combination, the semi-continuous experiments are carried out with e-Diesel as collector in the absence and presence of e-Montanol and Flotanol.

3.3 Semi-Continuous Flotation Experiments.

In soil remediation practice the effectiveness of the flotation result is based on the removal of the pollutant from the sludge. Optimal process conditions will lead to a clean sand phase that can be easily re-used as soil or building material and a small amount of contaminated froth that will need further treatment. The effectiveness of the semi-continuous flotation experiments is therefore based on the reduction of the PAH concentration in the sludge and on the percentage of dry matter of the treated sludge as compared with that of the foam. The results of the semi-continuous flotation experiments with the contaminated soil are presented in table 3.1. The results refer to the bulk material (silica tailing) in the sedimentation tank.

With e-Diesel but without either e-Montanol or Flotanol (experiment A1) the concentration of PAH in the tail is 14.2 mg/kg d.m. This is 56% of the PAH concentration in the original sludge (25.6 mg/kg d.m.), thus 44% of the PAH is removed. When the sludge is conditioned with e-Diesel in a 5% slurry instead of in a 25% (m/m) slurry, only about 13% of the PAH will end up in the froth (experiment A2). When e-Diesel is combined with Flotanol as frother (experiments B1 an B2), the removal of PAH increases to approximately 65%. When e-Diesel is added together with e-Montanol (experiments C1 and C2), around 84% of the PAH will be removed from the sludge by flotation. By adding extra Flotanol to the e-Diesel and e-Montanol (experiments D1 and D2), the removal of PAH stays at the same level of 84%. However, increasing the conditioning time of experiment C from 20 to 45 minutes enhances the removal of PAH with 11% up to 95% (experiment C3). Under these conditions the dry mass in the froth is equal to 2.8% of the dry mass in the sludge. Independent characterisation of the sludge, using polytungstate, showed that around 2.5% (m/m) of the sludge are soot particles. Comparison of these percentages indicates that the flotation process with e-Diesel plus e-Montanol selectively separates the soot particles from the sludge fraction. Finally it can be remarked that the silica fraction contains hardly any Diesel.

Table 3.1 Results of the semi-continuous flotation experiments on the soil sludge with an initial PAH concentration of 25.6 mg/kg d.m.

test	agent	dry matter (%) silica tailing	PAH (mg/kg d.m.) silica tailing	PAH removal (%)
A1	e-Diesel	99.04	14.2	44.4
A2[a]	e-Diesel	99.02	22.1	13.5
B1	e-Diesel and Flotanol	98.03	9.6	62.6
B2	e-Diesel and Flotanol	97.83	8.2	68.1
C1	e-Diesel and e-Montanol	98.57	4.0	84.4
C2	e-Diesel and e-Montanol	98.62	4.2	83.5
C3 [b]	e-Diesel and e-Montanol	97.95	1.4	94.6
D1	e-Diesel, e-Montanol and Flotanol	98.62	4.3	83.2
D2	e-Diesel, e-Montanol and Flotanol	97.20	4.2	83.7

[a] conditioned in 5% instead of 25% sludge (m/m),

[b] conditioned for 45 instead of 20 minutes

e = emulsified.

Summarising, the semi-continuous flotation experiments show that with the combination of e-Diesel and e-Montanol, the soot fraction in the sludge can be separated from the silica particles most effectively and that the concentration of PAH in the tail can be reduced from 25.6 mg/kg d.m. to 1.4 mg/kg d.m.. Part of the success is due to the conditioning process. A high particle concentration in the sludge and a relatively long conditioning step lead to the best results. This suggests that coagulation of the soot particles is important prior to the flotation.

3.4 Conclusion

Soot particles can be separated from silica particles by dissolved air froth flotation. This behaviour corresponds with the lower contact angle of silica compared with that of soot particles. DPC has a negative effect on the selective separation of soot from silica by flotation. This behaviour is in accordance with the contact angle measurements and the recovery tests of silica or soot in the presence of DPC. Aerophine increases the contact angle on the soot particles only slightly, but the flotation yield is substantially enhanced. Diesel, Biodiesel or n-hexadecane have also a positive effect on the flotation of soot, although the contact angle is hardly affected. Clearly the enhancement of the flotation results cannot be explained by changes in contact angles only. Most probably the enhancement is also due to a decrease in the stability of the soot particles, leading to coagulation of the soot particles and a better flotation result.

The practice-oriented and semi-continuous flotation tests show that a combination of emulsified Diesel and emulsified Montanol gives excellent results in terms of PAH (soot particle) removal, especially when the particle concentration in the sludge and the conditioning time before flotation are relatively large.

4

Flotation of PAH-Contaminated Dredged Sludge

Abstract The applicability of dissolved air flotation to remediate contaminated sediments of “Overschie” (Rotterdam) and “Petrol Harbor” (Amsterdam) is studied. Several flotation reagents (Diesel Fuel, Montanol, Aerophine, Aerofroth) are applied to enhance the flotation efficiency. The physical chemical characteristics of the different particles in the presence of surfactants are investigated by contact angle measurements.

In the absence of reagents a one step batch flotation experiment removes around 85% of PAH from both sludges. The remaining tailings contain 92% and 83% of the total mass for the Overschie and the Petrol Harbor sludge, respectively. When reagents are added the efficiency of the process decreases. The remaining tailings contain only 80 to 60% of the total mass, whereas the PAH removal is not substantially enhanced and in some experiments even dramatically reduced.

Huib Mulleneers, Suzan Roubroeks, Harry Bruning, Wim Rulkens, Luuk Koopal (2000). In Surfactant-Based Separations (science and technology), ACS symposium series 740, J.F. Scamehorn and F.H. Harwell (editors), 248-259.

4.1 Introduction

Surface water from rivers, lakes, ponds, canals, harbors etc., cover large areas of the Netherlands. Most of the water courses need regular dredging. Besides maintenance, environmental aspects can also be a reason for dredging. At certain sites the sediment is so polluted from discharge of harmful and toxic substances that it forms a threat to the aquatic ecosystem. It is estimated that between 1991 and 2010 around 590 million m^3 will have to be dredged. From this amount 90 million m^3 is dredged for environmental and 500 million m^3 for nautical reasons. The total amount of slightly to heavily contaminated sediment from these dredge activities is 250 million m^3 (Hofstra 1995). Contaminated dredged sediments cannot be reused and have to be cleaned or stored. Deposition is the cheapest method, however, with the present quantities of dredge sludge only a temporarily solution. Therefore treatment, for example, in the form of sand reuse or microbial degradation of the harmful substances, is necessary. The goal of the Dutch government for the year 2000 is treatment of 20% of contaminated dredged sediment. Remediation of sludge by classification is possible but the fraction below 63 µm, which is likely present in dredged sediments, may cause difficulties (Werther et al. 1990; Feenstra et al. 1995; Rulkens et al. 1995; Cuypers et al. 1998). Flotation techniques have proven to be a successful alternative remediation technique, also for the fine fractions (Clifford 1993; Bilz et al. 1994; Wevers et al. 1995; Wilichowski 1995; Venghaus et al. 1998; Mulleneers et al. 1999).

Main pollutants in dredge sludge are Polycyclic Aromatic Hydrocarbons (PAH), which arise from incomplete combustion of organic material (Engbertsen et al. 1988). They are mostly present in the form of soot or coal-tar particles and their selective separation from sand by flotation resembles to some degree coal flotation (Osborne 1988; Peng 1996).

Flotation techniques have been used in mineral processing for already almost 100 years (Jameson 1984; Kitchener 1984). The success of the flotation process is described by the product of collision efficiency, the attachment efficiency of particles and bubbles and the stability of the bubble particle aggregate (Derjaguin et al. 1961). In general, to enhance either or both the collision efficiency and the attachment efficiency and thereby the flotation efficiency, a “collector” is added. To enhance the stability efficiency “frothers” that produce a stable froth can be added (Leja 1982; Jones et al. 1984; Crozier et al. 1989). For inherently hydrophobic solids (coals, graphite, sulfur, molybdenite, talc), insoluble oil emulsified in water is often used as collector (Laskowski et al. 1992). The particle hydrophobicity is an important parameter for the attachment efficiency and therefore for the flotation efficiency itself (Fuerstenau 1957; Fuerstenau et al. 1972; Crawford et al. 1988; Subrahmanyam et al. 1996). The hydrophobicity of the particles can be quantified by the contact angle.

In this paper we focus on the remediation of two different types of dredged sediments, both contaminated with PAH. “Petrol Harbor” sludge is heavily contaminated, “Overschie” sludge is only slightly polluted. Earlier experiments have shown that soot particles can be selectively separated from sand by surfactant enhanced dissolved air flotation (Mulleneers, et al. 1999). Therefore the applicability of this technique, to remediate the contaminated sludges, is studied. The hydrophobicity of the different particles in the absence and presence of flotation reagents are investigated by contact angle measurements. The possibility of cleaning the two sludges with dissolved air flotation is tested in batch laboratory experiments.

4.2 Materials and Methods

4.2.1 Chemicals and Water

The inorganic chemicals used were of analytical grade. The water used for the contact angle measurements was demineralized using a mixed bed ion exchanger. Ordinary (non chlorinated) tap water was used for the flotation experiments. The hardness of the tap water based on the total Mg^{2+} and Ca^{2+} concentration was 0.79 mmol/l.

4.2.2 Flotation Reagents

Aerophine 3418a, a commercial collector, is a 50% aqueous solution of sodium di-isobutyldithiophosphinate and Aerofroth 76a, a commercial frother, is a mixture of C4-C7 alcohols. Aerophine and Aerofroth were obtained from Cytec Industries B.V. Aerophine is suggested for the flotation of gold and silver and can be combined with Aerofroth, which is useful whenever a light yet lively frothing action is desired. Montanol 350, a fluid mixture of mainly higher alcohols and esters with additives was obtained from Hoechst A.G. (Germany). Montanol 350 is especially developed for the flotation of coal (<0,5 mm). Diesel Fuel is a technical grade oil composed mixture of C15-C25 alkane chains with additives. The use of an oil is also derived from coal flotation (Laskowski and Ralston 1992). In order to facilitate the dissolution of Diesel Fuel and Montanol, emulsions were prepared by blending 1 ml Diesel Fuel or 1 ml Montanol in 99 ml water with 1 ml of a 0.1 g/l Eumulgin ET 10 solution. Eumulgin ET 10 is a commercial ethoxylated fatty alcohol obtained from Henkel A.G. (Germany).

4.2.3 Sludges

Both sediments were obtained from “Oost baggerdepot” deposit in Den Helder, The Netherlands. Fractions with a particle size between 45-90 μm were studied. These fraction were obtained by sieving the wet sediments on Retsch sieves. “Overschie” sludge (Rotterdam), was slightly polluted with PAH and oils. The “Petrol Harbor” sludge (Amsterdam) was heavily polluted. Both fractions contained mainly silica and organic matter. The organic matter was present as oil, coal-tar particles and natural organic matter (humus).

4.2.4 Contact Angles

The contact angles were determined on sessile drops using a contact angle microscope with goniometer (Erma Contact Angle Meter G-1). No special precautions were taken to control the humidity and vapor pressure. The contact angle on the organic fraction of the sludge was measured on pellets of this material, pressed at 14000 kg/m^2. The sand fraction could not be pressed into stable pellets and therefore, like in a former study, clean oxidized silicon wafer strips from Wacker chemitronic (Germany) were used (Mulleneers, et al. 1999).

Pre-isolation of the organic matter from the two sludges, for the production of pellets for the contact angle measurements, was achieved by sieving and upflow separation. The effect of size and therefore weight on the upflow separation was minimized by sieving the 45-90 µm fractions of the sludges into two fractions of 45-63 µm and 63-90 µm. From the separated fractions the organic matter was isolated by upflow separation in tap water. The used upstream velocity to separate the organic particles of the 45-63 µm fraction was 0.105 cm/s and for the 63-90 µm fraction it was 0.115 cm/s. The obtained organic fractions (45-63 µm and 63-90 µm) were finally mixed together to obtain one fraction again (45-90 µm). The organic matter content of the obtained “organic fraction” of Overschie was 58.5%, and that of the “organic fraction” of Petrol Harbor 68.5%.

Before every experiment the silicon wafer strips were washed with acetone and water followed by a 30 minutes treatment with ozone/UV. After the experiments the strips were cleaned by thermal oxidation or chromic acid. The organic pellets were used as pressed and could not be cleaned by addition of chemicals neither by oxidation.

4.2.5 Flotation Tests

For the flotation experiments a modified Hallimond tube (see Figure 4.1) was used. The tube has a narrow part near the bottom of the cell to decrease the turbulence in the middle part. The top part of the tube makes an angle of 60^o with lower part to assure a better settling of entraint particles. Before entering the sludge sample in the Hallimond tube, it was conditioned in a beaker by stirring approximately 6 grams dry matter (6 g d.m.) in 40 ml of solution for 30 minutes. This conditioning step was done for all experiments, i.e. also when no flotation reagents were added. Diesel Fuel and Montanol additions were 50 µl per 6 g d.m.. The applied Aerophine dose was 43 µl per 6 g d.m. and the Aerofroth dose is 86 µl per 6 g d.m.

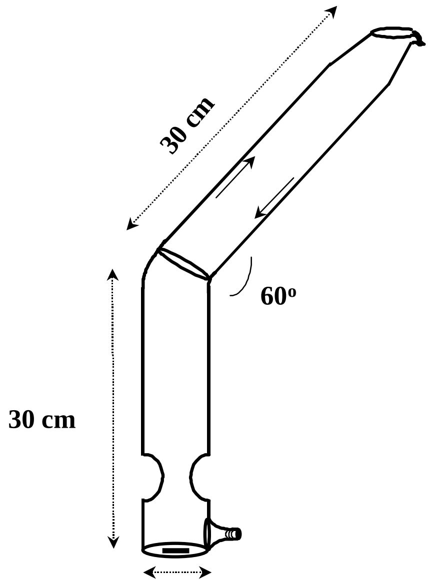


Fig 4.1 Hallimond type flotation tube

After conditioning the slurry was transferred into the flotation tube and the tube was filled up with water. The flotation was carried out by feeding pressurized water with dissolved air (7 bar) into the cell (100 ml/min) for 9 minutes. The floated particles were collected in a buchner funnel and dried at 50^o C. The tailing and the floated fraction were both analyzed for dry matter and organic matter, the tailings were also analyzed for PAH concentration.

4.2.6 Organic Matter Analysis

Approximately 0.3 grams of dried material (50^o C) were sampled and oxidized in a oven were the organic matter is oxidized at 550^o C for 18 hours. The organic matter content was determined by the difference in weight between the dried and oxidized matter.

4.2.7 Oil Analysis

Approximately 15 grams of dried (50^o C) sludge was extracted with an acetone/hexane mixture. The hexane was separated from the acetone and purified with Florisil and sodium sulfate. The oil concentration in the purified hexane was analyzed on a Hewlett Packard 5890 gas chroma-tograph, with a simdist column of 10 m and a diameter of 32 mm. After injection of 5 µl hexane the temperature was kept constant (40^o C) for the first 5 minutes. After this period it was linearly increased to 300^o C in 25 minutes. Finally the temperature was stabilized at 300^o C for the last 6 minutes. The oils were detected with a Flame Ionization Detector (FID). The total oil concentration was determined by a manual integration method.

4.2.8 PAH analysis

The samples were dried (50° C) and extracted with a 99% 1-methyl 2-pyrrolidinone solution. The concentrations of 16 PAH selected by the Environmental Protection Agency (USA) (16 EPA-PAH) were determined in the sample extracts. The separation of the 16 EPA-PAH was achieved by using a HPLC column with a length of 250 mm and a diameter of 4.6 mm, filled with Vydac 201TP54, a C18 reversed phase matrix, and eluted with a mixture of acetonitrile and degassed water (flow rate : 1.0 ml/min). The composition of the mobile phase was changed during elution: first a 50/50% (v/v) mixture of acetonitrile concentration and water for 5 minutes subsequently, the acetonitrile was linearly increased to 100% in 15 minutes, after which the acetonitrile concentration was kept at 100% for 19 minutes. The 16 EPA-PAH were measured with a photodiode-array detector and identified in the chromatograms by manual comparison of the sample spectra with that of the 16 standard EPA-PAH.

4.3 Results

4.3.1 Sludge composition

The PAH concentration, organic matter content and oil concentration of the two sludge samples are presented in table 4.1.

Table 4.1 PAH-, Oil concentration and Organic Matter content of Overschie and Petrol harbor sludge

	Overschie	Petrol Harbor
PAH concentration (mg/kg d.m.)	24	1035
Organic Matter percentage (%)	6.0	6.6
Oil concentration (mg/kg d.m.)	46	>1000

Table 4.1 clearly shows that the Petrol Harbor sludge is highly contaminated with PAH and oil, and Overschie relatively weakly. However, the organic content of both samples is comparable and much higher than the PAH and oil content, indicating that also a lot of humus type substances are present.

4.3.2 Contact Angels

The used droplets have a diameter of approximately 2.5 mm. The blank wetting solution contains 0.01 M NaCl and has a pH of 6. In the case of Diesel Fuel, Montanol and Aerofroth the blank solution is saturated with these fluids at 25° C. Aerophine concentrations range from 2 µl/l to 2 ml/l.

The results of the contact angle measurements are shown in table 4.2.

Table 4.2 Contact angles on silica pellets and organic pellets of Overschie and Petrol Harbor sludge

	Silica	Organic pellets Overschie	Organic pellets Petrol Harbor
Blank	4	79	90
Diesel Fuel	18	80	90
Montanol	26	57	76
Aerophine	7	80	92
Aerofroth	9	57	69

The contact angles reported in table 4.2 are averages of 3 measurements. The standard error in the measurements is about 3^o. However, it should be noted that the contact angle on the organic pellets are difficult to measure because the pellets are slightly porous and the droplets slowly absorb in the organic pellets absorb in the pellets. For Overschie pellets the absorption becomes noticeable after 30 seconds and for the Petrol Harbor after 60 seconds.

The contact angle of the blank solution on silica is 4^o, showing that pure silica is wetted very well. The values of 79^o and 90^o for respectively the Overschie and Petrol Harbor samples indicate that the organic particles are fairly hydrophobic. When saturated solutions of Diesel Fuel are used the contact angle on the silica plates raises to 18^o but those on the organic pellets remain the same within the experimental error. The effect of Aerophine over the studied concentration range is the same for all concentrations. The contact angle on silica is slightly enlarged to 7^o. The contact angle on the organic pellets of Overschie and Petrol Harbor are hardly effected and the average values are 80 and 92^o respectively. The saturated solution of Montanol decreases the contact angle on the organic pellets substantially, for the Overschie the angle is 57^o and for Petrol Harbor it is 76^o. To the contrary, Montanol increases the contact angle on silica is considerably to 26^o. These values indicate that Montanol is probably a very poor flotation reagent for the present system. Saturated solutions of Aerofroth show also a decrease of the contact angle on both the Overschie pellets (57^o) as well as on the Petrol Harbor pellets (69^o). However, the contact angle on the silica plates is only slightly increased to 9^o by the Aerofroth solution.

Because of the porosity of the organic pellets, contact angles larger than 80o or 90o, like the blank solutions, are hardly possible. Besides that the contact angle of the blank solutions on the silicon wafers is extremely small. Therefore, only the negative influence of reagents, by which the contact angle on organic pellets decreases and those on silicon wafers increases, can be notified.

4.3.3 Flotation Tests

The efficiency of the flotation process is determined by the removal of PAH from the sludges and the selectivity of this removal. This means that the PAH concentration in the tailings has to be very low and that the total mass of the tailing should be large. The final aim of the process is that the tailings can be reused as soil additive or building material and that the small but highly contaminated floated fraction can be treated by incineration.

To determine the flotation efficiency, the total dry matter (d.m.) and the organic matter of the floated fraction and tailings are measured. The PAH concentration in the tailings is measured too.

4.3.3.1 Overschie

The results of the flotation tests with the dredged sediment of Overschie are presented in Figures 4.2 and 4.3.

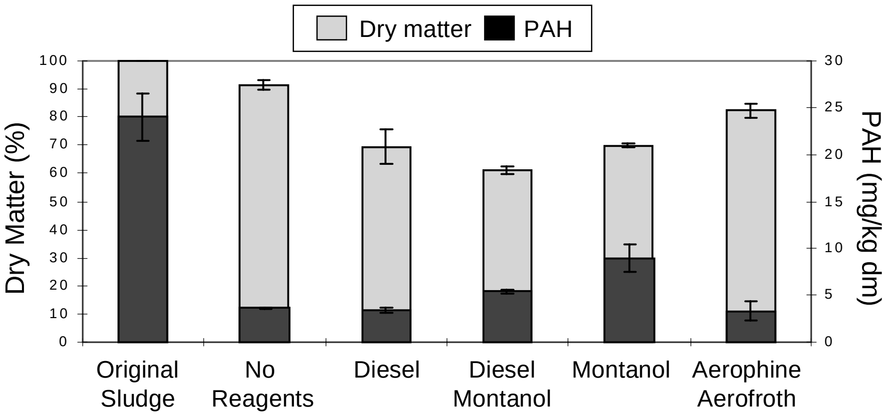


Fig 4.2 *PAH concentration and dry matter percentage of the tailings and the original Overschie sludge*

The original sludge contains 24 mg/kg d.m. PAH and of course 100% dry matter. When no flotation reagents are added the tailings contain 92% of the total mass and 3.6 mg/kg d.m. PAH which is 15% of the total PAH concentration. Addition of the reagents, Diesel Fuel, Montanol or the combination of Diesel Fuel and Montanol to the solution reduce the flotation efficiency. The removal of PAH in the experiment with Diesel Fuel (residual PAH are 3.4 mg/kg d.m.) is slightly better than with the blank but the dry matter content is only 70%. In the experiments with Montanol and Montanol combined with Diesel Fuel the residual PAH concentrations in the tailings are 5.4 and 9.0 mg/kg d.m.. Both values are higher than in the experiment without reagents and also the percentage of dry mass of the tailings are smaller

(60 and 70% respectively). Therefore, the efficiency is considerably decreased due to the addition of these reagents. The experiment with the combination of Aerophine and Aerofroth shows a tailing that contains 83% of the total dry mass and a PAH concentration of 3.3 mg/kg d.m.. This means these experiments were more successful than the experiments with Diesel Fuel and/or Montanol. In comparison to the tests without reagent the PAH removal is slightly better but the dry mass in the tailings is lower.

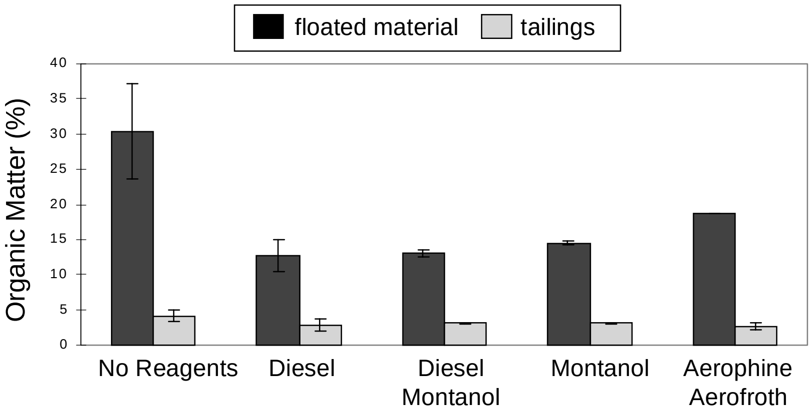


Fig 4.3 *Organic Matter content of both the tailings and the floated material of Overschie Sludge*

The poor efficiency of experiments with reagents is reflected in the low organic matter content of the floated material in relation to that of the experiment without reagents. The organic matter content of the floated material in absence of a reagent is 30% (Figure 4.3), whereas these values range from 12-14% for the experiments with Diesel Fuel and/or Montanol. The combination of Aerophine/Aerofroth gives, with 18% d.m., only a slightly better result and is still considerably lower than the 30% of the tests without reagent. The organic matter content of the tailing of the experiment without reagent is with 4% slightly higher than the organic matter contents (2 to 3%) of the experiments in which a reagent was added. However, as mentioned before the PAH concentration in the tailings are similar or higher. This suggests that there is no direct correlation between the PAH concentration of the tailings and the organic matter content. This is due to the fact that the organic matter is build up from coal-tar particles and natural organic matter. The coal-tar particles that contain the PAH are probably floated more selectively than the natural organic matter.

4.3.3.2 Petrol Harbor

The results of the flotation experiments with this sludge are presented in Figure 4.4 and 4.5.

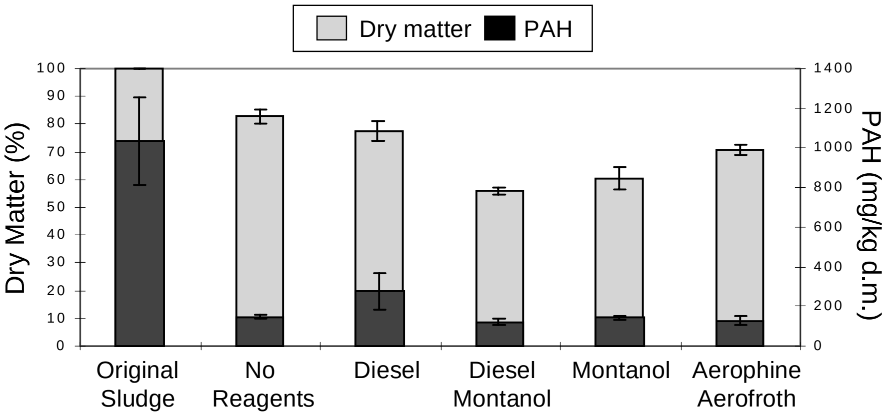


Fig 4.4 *PAH concentration and dry matter percentage of the tailings and the original Petrol Harbor sludge*

The original sludge contained 1035 mg/kg d.m PAH. Without flotation reagents the dry weight of the non-floated tailing is 83% of the total d.m. and it contains 148 mg/kg d.m. PAH, which is a reduction of 86%. Adding Diesel Fuel decreases the efficiency. The percentage dry matter in the tailing is only 78% and the PAH concentration as much as 280 mg/kg d.m. This shows that only 73% of the PAH is removed. Addition of Montanol and Diesel Fuel + Montanol leads to similar PAH removal as with the blank solution but also larger amounts of dry material (~ 40%) are removed, i.e. the process is less selective than in the absence of an reagent. The flotation in the presence of Aerophine and Aerofroth show a similar behavior, a good PAH removal (87%), but with a tailing of 70% d.m only a modest selectivity.

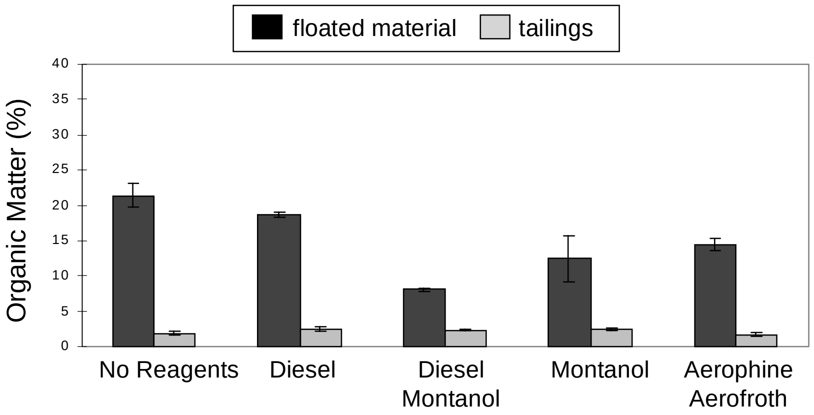


Fig 4.5 *Organic Matter content of both the tailing and floated material of Petrol Harbor sudge*

Similar as with the Overschie sludge the relatively poor selectively in the presence of Montanol, Diesel Fuel + Montanol, or Aerophine + Aerofroth is reflected in the low organic matter content, ranging from 8 to 14% of the floated part as compared with to the 22% observed in the experiments without reagents.

4.4 Discussion and Conclusion

For both sediments the tests without chemicals were the most successful. With Aerophine and Aerofroth the PAH removal could be increased but the selectivity is decreased. The effect of Diesel Fuel and Montanol on the flotation results was not the same for both sludges. In both sludges the efficiency of the flotation test was decreased but the poorest results in the experiments with the Overschie sludge was obtained when only Montanol was added and for the Petrol Harbor sludge when only Diesel Fuel was applied.

The fact that the applied chemicals do not enhance the flotation efficiency compares rather well with the results obtained for the contact angles. Without reagents the difference between the contact angle on the organic pellets and that on the silica plates was larger than with the reagents present. Especially the frother Montanol reduced the difference in contact angle substantially and this phenomenon is clearly reflected in the poor selectivity of the flotation experiments with Montanol. Also the other frother Aerofroth decreased the contact angle of the organic pellets. Therefore frothers should not be used in the conditioning step but should only be applied to the dissolved air stream to create a froth in the reactor.

That the PAH containing fraction of the sludges floats naturally is probably also due to the initial oil concentration in the sludges. Especially in the Petrol Harbor sludge the influence of the collectoric qualities of the oil makes it redundant to add an extra collector in the form of Diesel Fuel.

5

Selective Separation of Fine Particles by a New Flotation Approach

Abstract Fine particles often create problems in flotation applications. In this paper a new laboratory flotation system for the selective separation of small particles was designed and tested. The device contains an active counter current sedimentation that should prevent entrainment of the fine hydrophilic particles. The cell was used to selectively float fine particles in the size range of 2-25 µm. To create small bubbles Dissolved Air (DA) was used.

The study is linked to the problems that fine particles create by remediating soils and sediments. Therefore, small silica and small oxidized carbon black (MT-OX) particles were used as model system. Three different frothers, Sodium Dodecylsulfate (SDS), Aerofroth and Montanol were applied to obtain a stable froth.

The results showed that the equipment works excellent to separate the fine MT-OX particles from the small silica particles. Especially with Aerofroth as frother, the Grade of the flotation experiments was extremely high (98.1%). The MT-OX Recovery was best with SDS (74.6%). The new flotation design provides a promising method for the remediation of contaminated sediments and soils. Next to that it offers an interesting option to separate fine particles and powders in other industrial applications.

Mulleneers, H.A.E., Bruning, H, Rulkens, W.H., Koopal, L.K. Separation Science and Technology (submitted)

5.1 Introduction

Flotation is a separation technique based on the capture of particles by bubbles and their collection in a froth layer. It has already been used in the mining industries for more then 100 years (Ives 1984). Nowadays, it has also found its way in many other applications like wastewater treatment (Ives et al. 1995), plastic separation (Shibata et al. 1996), soil and sediment remediation (Wilichowski 1995; Cauwenberg et al. 1998; Cauwenberg et al. 1998; Venghaus et al. 1998; Venghaus et al. 1998; Wilichowski et al. 1998; Mulleneers et al. 1999; Mulleneers et al. 2000) and deinking of paper (Fischer 1982; Flynn 1983).

Efficient capture of bubble and particle can only occur when they undergo a close encounter, which is governed by the hydrodynamics in the reactor. When they approach within the range of attractive forces, film drainage, film rupture and contact line movement occur, a stable particle-bubble union is formed. Therefore, the particle may be dislodged from this state if it is supplied with sufficient kinetic energy to equal or exceed the detachment energy. The capture efficiency of a bubble and a particle may be defined as the product of the collision efficiency, the attachment efficiency and the stability efficiency (Derjaguin et al. 1961; Ralston et al. 1999).

Separation of small particles or fines often cause problems in flotation. Fines in flotation are mostly not only colloidal particles but are defined as all particles below 10 µm (Trahar 1981). Factors like, entrapment, entrainment, high specific surface areas and froth stabilization lead to reduction in efficiency and/or selectivity (Trahar 1981; Kirjavainen 1996).

Entrapment problems occur when fine hydrophilic particles (gangue) become physically trapped by hydrophobic particles or bubble-particle aggregates. Problems stemming from entrapment are sometimes reported as relatively minor (Fiscor 1992). However, the general view is that it is a main cause for high gangue recoveries (Kirjavainen 1996).

Hydraulic entrainment occurs when particles are recovered in the liquid film between air bubbles in the froth. Entrainment becomes prominent when large quantities of fine particles are treated (Fiscor 1992). The recovery due to entrainment will increase with water recovery, fine particle size and high slurry density (Johnson et al. 1974; Warren 1984). It has been suggested that the concentration of non-settling gang in the froth aqueous phase is equal to the concentration of the gangue in the pulp from which the froth is generated (Hemmings 1980; Hemmings 1981). Entrained gangue particles are able to drain back into the pulp via the network of channels formed by the interface bubble water. The coarser particles tend to drain from the froth more rapidly than the fines and there is consequently very little entrainment of siliceous gangue coarser than 30 µm. (Johnson, McKee et al. 1974; Trahar 1981).

Small particles also tend to have large specifics areas, which can lead to excessive adsorption of reagents, and other effects associated with chemically active particles (Warren 1984; Feng et al. 1999). Next to that, small particles show slow recovery rates, owing to decreased particle-bubble collision leading to a low rate of attachment (Trahar et al. 1976; Feng and Aldrich 1999). Furthermore, small hydrophobic particles will have a stabilizing effect on the structure of froth (Warren 1984; Bayraktar et al. 1998), however at very low concentrations fine hydrophobic particles could destabilize the froth (Kirjavainen 1996).

In coal treatment very fine particles, e.g. clay, often detoriate the yield and ash-content of floated coal. Therefore, coal companies are constantly seeking ways to improve fine coal recovery and several studies are done to improve the performance of the process (Hussain et al. 1996; Hadley et al. 1999; Mohanty et al. 1999; Mohanty et al. 1999).

Coals with a higher natural floatability only need a frother to float. In coal flotation the frothers not only act as bubblemaker, but according to Wheeler they also serve in a seldom acknowledged role of collector (Wheeler et al. 1987; Wheeler 1995).

To optimize the flotation of fine particles, small air bubbles and a low air flowrate are desired (Kirjavainen 1996; Ramirez et al. 1999). Small bubbles do always give a higher attachment efficiency than do larger bubbles. It has been shown that the increase in attachment efficiency, caused by a decreasing bubble size is more pronounced for smaller particles than for larger particles (Ralston, Fornasiero et al. 1999). Therefore it is always more effective to utilize small air bubbles for the flotation of small particles.

An elegant way to create small bubbles is the use of dissolved air. Dissolved Air Flotation (DAF) is the process whereby small bubbles are precipitated when water, supersaturated with air under high pressure, is released under atmospheric conditions. It is mainly used in the field of wastewater treatment (Haarhoff et al. 1993; Edzwald 1995)

The micro-bubbles formed by DAF have a diameter generally between 10 and 120 µm and a reasonable estimate of the average bubble diameter is 40 µm (Edzwald 1995). Additional bubble growth may occur as the bubbles rise in the flotation tank due to a decrease in the hydrostatic pressure or by coalescence. Both of these have negligible effects on the small bubbles formed in DA systems. Besides that the coalescence of bubbles on the walls of hydrophobic tubes leads to the formation of macro-bubbles (Edzwald 1995; Ponasse et al. 1998). The formation of these bubbles greater than 500 µm, seems to be linked with the process of DAF and is often observed by the users of dissolved air flotation (Dupre et al. 1998).

In this research we test a new designed flotation device for its ability to selectively float fine particles. In general our research is linked to the remediation of contaminated soil and sediment. For the remediation of the smallest particle fractions of them there is no appropriate classification technique available. Flotation appears to be a promising alternative for the separation of soot type particles, containing Polycyclic Aromatic Hydrocarbons (PAH), from the sand particles (Mulleneers, Koopal et al. 1999). Therefore, a model system that simulates a contaminated sludge composed of very small soot/coal-tar particles and small sand particles is simulated. In this model system oxidized carbon black particles represent the soot/coal-tar particles and pure silica the sand and clay fraction. The carbon black sample and silica sample are both in the particle size range of 2-25 µm. Three different types of frothers are tested and their influence on the grade and recovery is calculated. Because coals often only need a frother to float no collector is added. Dissolved air is used as bubble source.

5.2 Experimental

5.2.1 Materials

5.2.1.1 Reagents

Three different frothers were used, a lower alcohol (Aerofroth 76a), a higher alcohol (Montanol 350a) and low budget sulphonated agent (Sodium Dodecylsulfate).

Sodium Dodecylsulfate (SDS) was obtained from Aldrich. Aerofroth 76a, a commercial mixture of C4-C7 alcohols, was obtained from Cytec Industries B.V. (the Netherlands). Montanol 350, is a mixture of mainly higher alcohols and esters with additives, and was obtained from Aventis (formally Hoechst A.G. (Germany)). Montanol was emulsified with Eumulgin ET 10, a commercial ethoxylated fatty alcohol obtained from Henkel. The emulsion was obtained by intensively blending 5 ml Montanol in 41 ml demineralized water with 4 ml of a 0.1 g l^{-1} Eumulgin solution. Flotation experiments were carried out with tapwater. The hardness of the tapwater based on the total Mg^{2+} and Ca^{2+} concentration was around 0.8 mmol/l.

5.2.1.2 Small particles

To get a well defined sludge of silica and carbon black, two specified types of small particles were used.

Oxidized carbon black particles denoted as MT-OX were obtained by oxidation of Sterling MT carbon black obtained from Cabot (USA). Prior to the oxidation, the particles were cleaned by extraction in toluene. The oxidation was carried out with 100 g carbon black in 800 ml 2M HNO_3 for 6 hours at 75°C. After oxidation the degradation products were removed by extensive rinsing with subsequently demineralized water, 1% Na_2CO_3 solution and again with demineralized water. The thus obtained suspension is washed with 0.1 M HCl to exchange the Na^+ counterions for H^+ and washed with demineralized water again. The final MT-OX is dried and stored in a closed container.

Before use, the MT-OX is redispersed in water by ultrasonification in order to break down large particle aggregates into small aggregates. Due to the oxidation step acidic surface groups are formed (about 20 µmol/g) and this facilitates the dispersion in aqueous solutions.

For the ultrasonification step 5 grams of MT-OX were mixed in a beaker with 500 ml of tap water and ultrasonificated for 15 minutes using a Elam Transonic T700 (35 kHz). The ultrasonified MT-OX particle aggregates had a diameter of around 4 µm. Although the treatment was successful, the presence of some large particle aggregates in the ultrasonified MT-OX could not be avoided.

Silica gel (28,8500-0) was obtained from Aldrich. The size range of the silica particles was as quoted by Aldrich is 2-25 µm.

Three slurries were tested, MT-OX, Silica and MT-OX/Silica. The MT-OX slurry contained, 5 g of the ultrasonified MT-OX, the Silica slurry contained 25 g silica and the MT-OX/Silica slurry contained 25 g silica plus 5 g ultrasonified MT-OX in 500 ml water.

5.2.2 Methods

5.2.2.1 Flotation device

The flotation equipment in this study is presented schematically in figure 5.1. Two new ideas were incorporated. Like in a former study (Mulleneers et al. 1999), the mixing zone is followed by a tilted zone that is extended in length to allow a better settlement of entrapped and entraint particles. Next to this, the mixing zone and the sedimentation zone are separated by baffle Y that prevented that settled particles fell back in the mixing zone of the reactor. The settled particles were drained away in an additional effluent stream as in the Rubio cell (Rubio 1996) and there is no accumulation of fine hydrophilic particles in the cell. Furthermore, the separation of the mixing compartment and sedimentation compartment created an active counter current sedimentation flow which improves the settling velocity of the hydrophilic particles even more.

5.2.2.2 Dissolved air solution

Water was saturated with air in a saturation tank (5 l) at a pressure of 8 bar. It was released to atmospheric pressure in the flotation cell through an adjustable Hoke nozzle, creating small bubbles of 10-100 µm.

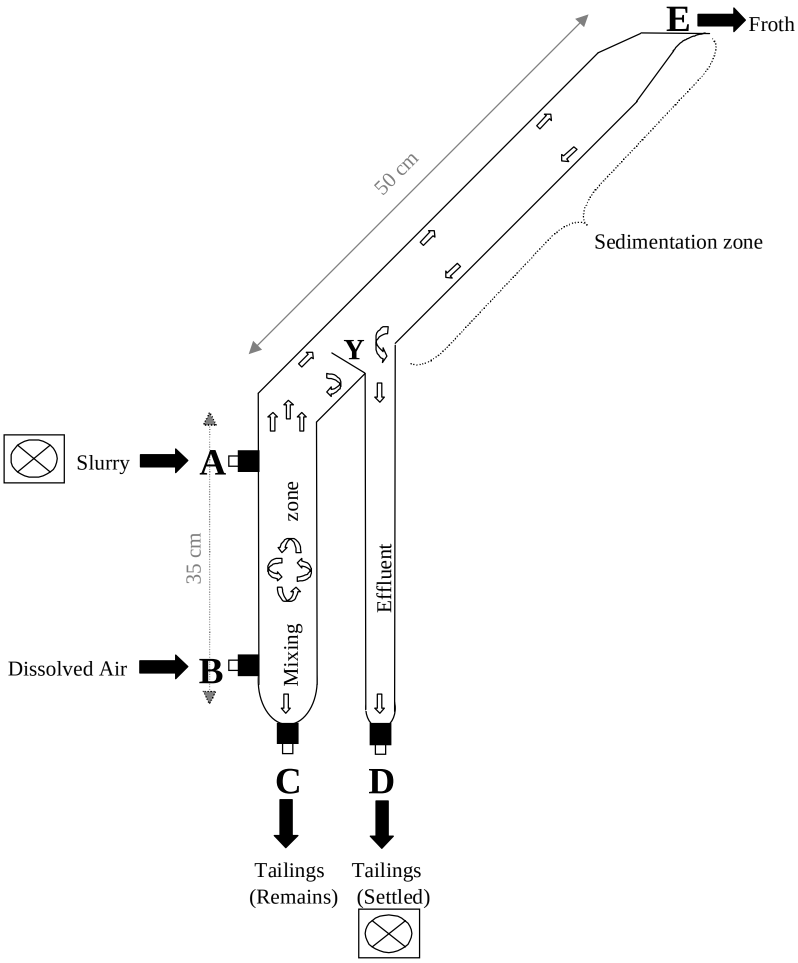


Fig 5.1 *Counter current flotation sedimentation column*

5.2.2.3 Flotation procedure

After ultrasonification and prior to flotation the conditioning of the slurry started by stirring with a magnetic stirrer. Before the slurry was fed into the mixing compartment at point A (30 ml/min) the flotation cell was filled with water. The DA flow was started at point B (90 ml/min), two minutes prior to the sludge flow. During the flotation the effluent was removed as “Froth” at point E or as “Settled” at point D. The valve at C remained closed till the end of the experiment. The flow at point D was set equal to the flow of pump A plus the DA flow at B so that the water level at point E was constant. Each minute the froth was manually removed from the top by a spoon. If no froth occurred a very small overflow (~5 ml/min) was created, but also the particles floating at the top were once a minute manually removed.

During the experiment, the wall of the influent beaker was rinsed regularly to remove the particles attached to the glass. When the influent was almost finished, water was added to remove also the last particles from the beaker. In total 250 ml water was added for rinsing. When the influent flow was finished, the DA flow was continued for 10 minutes wereafter the experiment was stopped. After the experiment the slurry in the mixing part was collected as “Remains”. The slurry in the sedimentation tube was added to the Settled particles. In this way three fractions were collected, Froth, Settled, and Remains.

5.2.2.4 Analyses

All samples were dried at 95^{o}C to determine the dry matter content. Subsequently the organic matter content was determined by oxidation dry matter samples in a oven at 550^{o}C for 24 hours.

5.2.2.5 Grade and Recovery

The organic content of the samples reflects mainly the MT-OX content. For the precise calculation of both the amount of MT-OX and Silica in each sample the organic content of silica (2.6%) and MT-OX (99.5%) have been taken into account. With the known amounts of MT-OX and Silica in each of the fractions the grade and recovery have been calculated as:

$$\text{Grade} = \frac{\text{amount of MT - OX in froth (g)}}{\text{dry matter in froth (g)}} \text{X} \, 100\% \qquad \text{(iii)}$$

$$\text{Recovery} = \frac{\text{amount of MT - OX in froth (g)}}{\text{amount of MT - OX in Settled, Froth and Remains (g)}} \text{X} \, 100\% \qquad \text{(iv)}$$

5.3 Results and Discussion

5.3.1 Frother Addition

Screening tests were done to find, the minimum concentration of frother that is necessary to create small bubbles and a stable froth. To this aim different frother amounts were tested. Frother was added to either the influent water or to the water in the saturation tank before air saturation.

The screening tests showed that addition of frother to the DA solution was much more efficient than addition to the particle slurry. With addition of frother via the DA solution, lower frother amounts were sufficient to create appropriate air bubbles and a stable foam. Also the formation of macro bubbles is substantially reduced with this way of frother addition. Minimum frother concentrations at which the formation of small air bubbles and a stable froth was achieved are presented in table 5.1.

Table 5.1 Minimum frother concentrations to obtain a stable foam and small bubbles.

Frother	SDS	Aerofroth 76a	Montanol 350
Concentration	0.028 g/l DA	0.017 ml/l DA	0.008 ml/l DA

In further experiments frother was always added with the DA.

5.3.2 Flotation Tests Of Pure Samples

The first flotation experiments were performed on the pure Silica and MT-OX samples. The entrainment of the small particles was measured and the influence of frother on the floatability of them was estimated.

The results for the Silica samples are shown in table 5.2 and those for MT-OX in table 5.3. The results show the distribution of mass over the three fractions. A certain amount of material could not be removed from the influent beaker or stayed in the influent tubes. Therefore, the total particle mass of the three fractions was always smaller than the particle mass in the original influent. The percentages given in table 5.2 and table 5.3 are thus based on the total amount in the three fractions.

Table 5.2 Mass distribution over the three fractions of Silica.

	Remains (%)	Settled (%)	Froth (%)
No frother	16	80	4
SDS (0.028 g/l DA)	17	81	2
Aerofroth (0.017 ml/l DA)	16	82	1
Montanol (0.008 ml/l DA)	18	81	1

Without addition of frother the froth layer was very thin and the bubbles showed little stability and collapsed mostly at point E. In this case a small overflow was maintained to be able to collect the particles from the top.

The results of the Silica samples show that the amount of silica that remained in the mixing compartment (Remains) was around 17% for all the experiments. The amount of silica that was collected in the Froth was very low. Without frother 4% was collected in the Froth, with SDS, Montanol or Aerofroth only 1 to 2%. The amount of silica that is carried out of the mixing compartment but settled in the sedimentation zone is large (~80%) and not effected by the frother. As silica should not end up in the froth the latter result shows the importance of the active sedimentation zone in the flotation equipment. The present device minimizes the entrainment.

Table 5.3 Mass distribution over the four fractions for the MT-OX sample experiments.

	Remains (%)	Settled (%)	Froth (%)
No frother	37	55	8
SDS (0.028 g/l DA)	15	49	36
Aerofroth (0.017 ml/l DA)	16	71	14
Montanol (0.008 ml/l DA)	17	72	11

The results of the MT-OX samples show that in the presence of frother the amount of MT-OX in the Remains was around 16%. When no frother was added the amount of MT-OX in the Remains equals 37%. This high value is reflected in the relatively low values for the Froth and the Settled fraction. Comparison of the 37% with the 16% indicates that the particle-bubble attachment efficiency is improved. Hence, the frothers also act as collectors.

The amount of MT-OX in the froth is very modest. This can be due to the hydrophilic groups present at the surface of MT-OX. Also the flotation device which is constructed to minimize the entrainment will be responsible for the low amount of MT-OX in the Froth. The experiment with SDS shows that 36% of the mass is in the Froth, this is 4 times more than in the absence of SDS. For the other two frothers the amount of mass in the froth is much less (11-14%). The high amount of mass in the Froth in the case of SDS leads to a relatively low amount (49%) of settled material. For Aerofroth and Montanol the amount of settled material is 71-72%. As the “Remains” are the same for the three frothers the results indicate that with SDS more stable particle/bubble complexes are formed than with Aerofroth and Montanol.

Due to the fact that MT-OX is not highly hydrophobic the particles will settle in the sedimentation zone unless an effective collector is present.

5.3.3 Flotation Tests Of Mixed Samples

To test the performance of the new flotation device, the particles were mixed and the separation efficiency was calculated by the Grade and Recovery. The results of the flotation tests are shown in table 4 and illustrated in figures 4 and 5.

The dry matter percentages given in table 4 are again based on the total dry matter in the three fractions. The MT-OX percentages are based on the amount of MT-OX in relation to the total amount of silica and MT-OX in that fraction. The amount of MT-OX and silica is calculated from the organic matter content of that fraction as explained in the methods. The values in the table are averages of duplicate experiments.

Table 5.4 Dry matter and MT-OX percentage in each of the MT-OX-Silica samples.

	Remains (%)		Settled (%)		Settled (%)	
	d.m.	MT-OX	d.m.	MT-OX	d.m.	MT-OX
SDS (0.028 g/l DA)	14.7	3.6	75.5	3.3	9.8	92.0
Aerofroth (0.017 ml/l DA)	19.5	5.3	70.9	7.6	9.6	98.1
Montanol (0.008 ml/l DA)	17.3	5.0	78.7	9.4	4.0	81.8

The results in table 5.4 show that the average amount of material in the Remains was 14.7% for SDS, 19.5% for Aerofroth and 17.3% for Montanol. These values are slightly higher than those of the pure samples. The MT-OX content of the Remains is 3.6% for SDS and around 5% for the experiments with Aerofroth and Montanol.

The relatively high dry matter percentage in the Remains of Aerofroth is reflected in the lower dry matter percentage of the Settled fraction (70.9%) compared to the amounts in the Settled Montanol (78.7%) and SDS (75.5%).

For SDS the lowest MT-OX contents are found in the Remains (3.6%) and Settled (3.3%) fractions. This corresponds with the better flotation of pure MT-OX in the presence of SDS.

The dry matter percentage of the Froth fraction in the presence of Montanol (4.0%) is lower that in the presence of Aerofroth (9.6%) and SDS (9.8%). Moreover, the MT-OX content in the Froth is for Montanol relatively low. The MT-OX values of the Froth fractions stand for the selectivity of the flotation process and are also presented as Grade in figure 5.2. The values of the duplicates are shown as arrow bars.

Fig 5.2 Grade in the presence of SDS, Aerofroth and Montanol

Figure 5.2 clearly show that the grade is high in all the experiments. With Aerofroth the grade was almost maximum, showing 98%. The grade with SDS is only slightly less but with 92% still very high. The grade with Montanol is substantially lower (82%) and as mentioned before the dry matter percentage is low.

The calculated Recovery is presented in figure 5.3, the figures show the averages, with the values of the duplicates presented by the arrow bars.

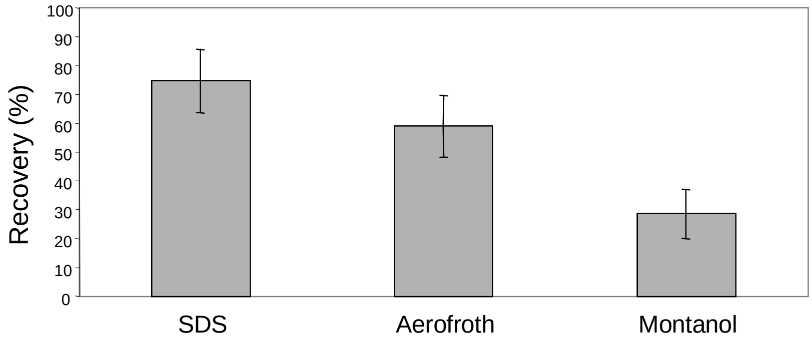


Fig 5.3 *Recovery in the presence of SDS, Aerofroth and Montanol*

The Recovery of the device is lower then the grade. As expected from the previous discussion the best Recovery (74.6%) is obtained with SDS. With Montanol only 28.5% of the MT-OX could be floated. The relatively poor results with Montanol are probably caused by the low particle/bubble stability and the low stability of the froth. With Montanol as frother a thin froth layer with a coarse structure and a high water content was created. The froth was unable to hold a sufficient amount of particles.

The Recovery with Aerofroth (58.9%) was, as expected from the pure sample experiments, lower than when SDS (74.6%) was used. Apart from the stability of the particle/bubble complex, the lower recovery of Aerofroth compared to SDS can also be explained by looking at the structure of both froths. The structure of the SDS froth was thicker and more stable than in the case of Aerofroth. Therefore, more particles were recovered.

A striking difference is noticed regarding the MT-OX Recovery with the pure (11-36%) and mixed (28.5-74.6%) samples. Apparently the higher particle density in the mixed samples results in a better flotation efficiency. As most particles are initially carried from the mixing to the sedimentation zone, a different settling behavior of the MT-OX particles must exist. Most probably the breaking and reformation of MT-OX particle/bubble complexes in the flotation sedimentation zone is affected by the overall particle concentration.

5.3.4 Silica concentration in Settled and Froth

For the experiments with SDS and Aerofroth as frother, the aqueous phases of the Froth fraction was around 200 ml. In the experiments with Montanol the froth was as mentioned before less stable and more water had to be manually removed (400 ml). The Settled fractions had a volume of around 5 l.

In figure 5.6 the silica concentrations of Settled and Froth are presented for the experiments with the MT-OX/Silica samples. The figures show the average silica concentrations with the values of the duplicates presented in the arrow bars.

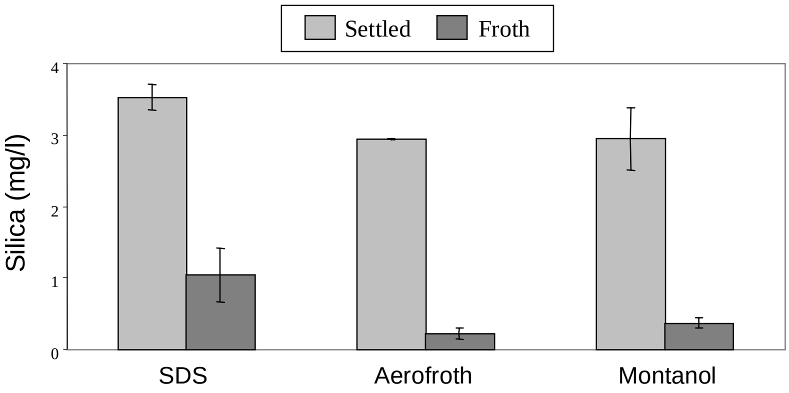


Fig 5.6 *Silica concentrations in the experiments with MT-OX-Silica samples*

The high grade with Aerofroth is reflected in the low silica concentration (0.2 mg/l) in the froth. For SDS the silica concentration in the froth (1.0 mg/l) is higher compared to Aerofroth and can be explained by the relatively higher recovery and lower grade. For Montanol the amount of silica is also relatively low (0.4 mg/l), but the volume of the Froth fraction is also larger.

The small silica concentrations in the Froth fractions compared to the concentrations in the Settled fractions are remarkable. Some flotation theories assume that the concentration of hydrophilic particles in the pulp is equivalent to the concentration of hydrophilic particles in the aqueous phase of the froth (Hemmings 1980; Hemmings 1981; Jowett 1983). Our results showed that the concentration in the Froth fraction were around 3 to 15 times lower than the suggested concentration.

5.4 CONCLUSION

By adding frother to the DA solution, instead of to the particle slurry lower frother amounts are sufficient to create small bubbles and a good froth stability.

Small silica and MT-OX particles are well suited to test selective flotation of fine particles.

The good Recovery and a very high Grade, show that the new reactor is an excellent device to selectively float fine particles. With an appropriate frother the small MT-OX particles could be separated from the small hydrophilic silica particles. The best recovery (74.6%) was obtained with SDS. The most selective separation was achieved with Aerofroth. The grade of 98.1% showed that entrainment and entrapment of silica was negligible, even for the very small particles used.

In relation to the remediation of contaminated soil and sediments it may be expected that also the finest fractions can be cleaned from soot or coal tar particles. Next to the application in the remediation of contaminated soil the flotation device, with a sedimentation zone and a prevention that the settled particles return to the mixing zone, is probably also an promising tool to separate fine particles and powders in other (industrial) applications.

6

Remediation of the Finest Fraction of Dredged Sediment by Flotation

Abstract In the Netherlands, large quantities of contaminated dredged sludge have to be deposited or treated in the near future. Especially the large amounts of small particles involved, make successful treatment difficult. In this study a new flotation method was used as alternative remediation technique. Dissolved air was used to create small bubbles. Laboratory tests were performed with the finest fractions of sediments of Overschie (Rotterdam) and Petrol Harbor (Amsterdam) sludges contaminated with Polycyclic Aromatic Hydrocarbons (PAH). Several agents and conditions were tested to enhance the flotation efficiency.

For Overschie sludge the best results were obtained without collector and SDS as frother. The PAH concentration in the Froth was up to 8 times higher than that in the fractions collected as Settled or Remains. The collected amount of dry matter in Froth was around 13%. With a two step flotation, the PAH concentration of the re-usable Settled + Remains fraction was reduced from 240 mg/kg d.m. to 99 mg/kg d.m.

For Petrol Harbor sludge the best results were obtained with the alcoholic frothers Aerofroth and Montanol. The flotation was less selective than with Overschie sediment. Around 50% of dry matter was collected in Froth and the PAH concentration in the Froth was around 2 times higher than in the Settled fraction and 3-5 times higher than in the fraction Remains.

Mulleneers, H.A.E., Mark van der, B.C., Geraets, J. Gelder, van B., Bruning, H., Rulkens, W.H., Koopal, L.K., (2001) Environmental Technology (submitted).

6.1 Introduction

Till 2010 approximately 425 million cubic meters of sediment from for example harbors, lakes and rivers have to be removed in the Netherlands. Around 25% of this sediment is contaminated and has to be treated (Groen 1999). Deposition is the common way to deal with the contaminated sludge. However, with the large quantities of dredged sludge this is only a temporarily solution. Next to that, most deposits need maintenance till the far future which will make them more expensive then has been assumed in the past. Therefore, remediation of the dredged sediment is necessary. Soil washing, which is the common way to deal with excavated contaminated soil (VvAV 1997), is the most obvious remediation technique.

With soil washing the soil is classificated into a clean reusable sand fraction and several contaminated fractions. The separation is done by techniques based on density and size of the soil particles using for example sieves and hydrocyclones (Neesse et al. 1991; Feenstra et al. 1995). Flotation is often used as refinement step for the smaller sand fraction (63µm-200µm) or in combination with flocculation to remove slime from the process water (Wilichowski 1994; Habil et al. 1995; Wilichowski 1995). Because the conventional classification techniques are not able to separate the smallest particles (<63µm), the smallest fraction is mostly not treated but some alternatives have been investigated (Pearl 1995; Pearl et al. 1996). Flotation is one alternative to remediate the smallest soil fraction (Mulleneers et al. 1999). Research on contaminated dredged sediment showed that flotation is also a promising technique for the remediation of small dredged sludge particles (Cauwenberg 1998; Mulleneers et al. 2000).

Like other classification techniques, also with flotation processes problems may occur when particles become significantly smaller than 63 µm. Regular flotation equipment is not adapted to float such small particles. The high turbulence and large bubbles in these reactors may cause entrainment and entrapment. Entrainment occurs when hydrophilic particles move with the waterflow and are recovered in the liquid film between air bubbles in the froth. Entrapment takes place when fine hydrophilic particles become physically trapped by hydrophobic particles or bubble-particle aggregates (Trahar et al. 1976; Kirjavainen 1996). The presence of entrainment and entrapment of small particles in conventional reactors make reactor modification necessary to minimize these phenomena.

In sediments of harbors, lakes, rivers and ponds Polycyclic Aromatic Hydrocarbons (PAH) are one of the most common pollutants. In general PAH arise from uncompleted combustion of organic material (Engbertsen et al. 1988). PAH bind preferentially to a higher carbon content matrix. They are mostly present in soot or coal-tar like particles (Osborne 1988; Peng 1996; Gillette et al. 1999). Flotation of these soot particles from the soil matrix resembles to some degree coal flotation. To enhance the hydrophobicity of coal, reagents are added. For lower ranks coals, often non polar oils like Diesel are used as collector. The oil sometimes is emulsified to create a larger surface and a better distribution over the slurry. Higher rank coals have a higher natural floatability and only need a frother to float. Aliphatic alcohols have shown to be the most successful frothers (Seitz et al. 1987; Wheeler et al. 1987).

The goal of the present research is to investigate the selective flotation of PAH containing particles from the finest fraction (32 µm) of dredged sediments. The separation technique should lead to two fractions. A contaminated fraction ending in the froth, which could be incinerated or dumped, and a clean reusable fraction ending in the tailings. Two different types of sediments were investigated, Petrol Harbor sludge (Amsterdam) and Overschie sludge (Rotterdam). Earlier experiments with these sediments have shown that PAH can selectively be removed from the fraction of 45-90 µm by Dissolved Air Flotation (Mulleneers, Roubroeks et al. 2000). The effect of two collectors and three different types of frothers is investigated. Moreover, it has been investigated whether or not a high soot content also corresponds with a high PAH concentration. The flotation is carried out with dissolved air in a newly developed cell (Mulleneers 2001).

6.2 Materials en Methods

6.2.1 Reagents

Ordinary (non chlorinated) tap water was used for the preparation of the sludge samples in the flotation experiments. The hardness of the tap water based on the total Mg^{2+} and Ca^{2+} concentration was around 0.8 mmol/l. The inorganic chemicals used were of analytical grade.
Three agents (SDS, Aerofroth 76a and Montanol 350) were used as frother and two agents (Diesel and Aerophine 3418a) were used as collector. Sodium Dodecylsulfate (SDS) was obtained from Aldrich. Aerophine 3418a, a commercial collector, is a 50% aqueous solution of sodium di-isobutyldithiophosphinate. Aerofroth 76a, is a mixture of C4-C7 alcohols. Aerophine and Aerofroth were obtained from Cytec Industries B.V. and can be combined.

Montanol 350, a fluid mixture of mainly higher alcohols and esters with additives, was obtained from Hoechst A.G. (Germany) and especially developed for the flotation of coal (<0.5 mm). Diesel Fuel is a technical grade oil composed mixture of C15-C25 alkanes with additives. The use of an oil is also derived from coal flotation practice. In order to facilitate the dissolution of Diesel Fuel, Montanol and Aerofroth, emulsions were prepared by blending 5 ml of agent in 41 ml water with 4 ml of a 0.23 g/l Eumulgin ET 10 solution. Eumulgin ET 10 is a commercial emulgator composed of ethoxylated fatty alcohols and obtained from Henkel A.G. (Germany).

6.2.2 Sludges

Both sediments were obtained from “Oost baggerdepot” deposit in Den Helder, The Netherlands. “Overschie” sludge (Rotterdam), was slightly polluted with PAH and oil. The “Petrol Harbor” sludge (Amsterdam) was heavily polluted with PAH and oil. Both fractions contained mainly clay, silt, sand, and organic matter (Cuypers 2001).

To obtain the small particle fractions of both sediments, the sediments were sieved over a 500 µm Retsch sieve. Thus obtained fractions were cycloned using a Mozley cyclone (C700 MKII). Overschie (Rotterdam) sludge was cycloned over a 3 inch stub cyclone at a pressure of 1.2 bar with a spigot of 15 mm and a vortexfinder of 25 mm. The underflow of the cyclonage is cycloned another time under the same condition. The two overflows were mixed and used as basic slurry A. With basic slurry A experiments O1 till O3 are performed. The process was repeated under the same conditions and another basic slurry (B) is created. With this basic slurry B the experiments O4 till O6 were performed.

Table 6.1 Particle diameters, Mass distribution, organic matter contents and PAH concentration of the slurries.

Slurry	Fraction (µm)	Mass (%)	Organic Matter (%)	PAH (mg/kg d.m.)
A (O1-O3)	>32	16.8	65.8	241.8
	<32	83.2	36.5	157.3
	Total	100	41.4	171.2
B (O4-O6)	>32	15.6	63.7	*
	<32	84.4	31.6	*
	Total	100	36.6	243.6
C (P1-P8)	<32	>99	19.1	1800

* not measured

The Petrol Harbor sludge was firstly cycloned by a 3 inch stub cyclone at a pressure of 2.4 bar with a spigot of 10 mm and a vortex finder of 25 mm. The overflow was cycloned by a 2 inch extended cyclone at a pressure of 1.2 bar with an spigot of 9.4 mm and a vortexfinder of 8 mm. The overflow of this step was cycloned again under the same conditions. The overflow of this last step was used as basic slurry C. With slurry C the experiments P1 till P8 were performed. The mass distribution, organic matter contents and PAH concentrations of slurries A, B and C are presented in table 6.1.

6.2.3 Flotation Tests

The flotation equipment used in this study is presented schematically in figure 5.1. Two new ideas are incorporated. Like in a former study (Mulleneers et al. 1999), the mixing zone is followed by a tilted zone that is extended in length to allow a better settlement of entrapped and entraint particles. Next to this, the mixing zone and the sedimentation zone are separated by baffle Y, that prevents that settled particles fall back in the mixing zone of the reactor. The settled particles are drained away in an additional effluent stream as in the Rubio cell (Rubio 1996) and there is no accumulation of fine hydrophilic particles in the cell. Furthermore, the separation of the mixing compartment and sedimentation compartment creates an active counter current sedimentation flow. Dissolved air (DA) is used as air supply. Water with frother is saturated with air in a saturation tank at a pressure of 8 bar during 20 minutes. At the start of the experiment the water is released to atmospheric pressure through an adjustable needle valve (Hoke) nozzle, creating small bubbles of 10-100 µm.

Slurry samples were taken from the slurries A, B or C and transferred to a beaker and diluted to 4% (m/m). Prior to flotation the conditioning of the slurry started by adding the collector (if applied) and stirring with a magnetic stirrer for 20 minutes. Before every experiment the cell was filled with water. Two minutes before the slurry was fed into the mixing compartment at point A, the DA was started at point B. Effluent was removed as “Froth” at point E or as “Settled” at point D. The valve at C remained closed during the experiment. The flow at point D was set equal to the total flow of pump B plus the DA flow, so that the water level at point E was constant. Every minute the froth was manually removed by a spoon. When the influent flow was finished, the DA flow was continued for 10 minutes wereafter the experiment was stopped. After the experiment the slurry in the mixing compartment was collected as “Remains”. The slurry in the sedimentation tube was added to the Settled particles. In this way three fractions were collected, Froth, Settled, and Remains.

6.2.4 Analyses

Dry matter and organic matter. All samples were dried at 95°C to determine the dry matter content. Subsequently the organic matter content was determined by oxidation of the dry samples in a oven at 550°C for 24 hours. For some experiments the total organic matter was subdivided into “natural organic matter” and “soot”.

According to Gustafsson (Gustafsson et al. 1997) natural organic matter can be distinguished from soot organic matter by thermal oxidation. At a temperature of 375°C natural organic matter is decomposed whereas soot organic matter remains intact. Therefore, the dried organic matter samples of O1 till O3 were oxidized in an oven at 375°C for 24 hours and the weight loss was measured (non-soot), subsequently the samples were further oxidized at 550°C for 24 hours and again the weight loss was measured (soot).

6.2.4.1 PAH extraction

Dried samples of experiments O1 till O3 were transferred into a 99% 1-methyl 2-pyrrolidinone solution Then the solution was ultrasonified (Elam Transonic T700, 35 kHz) for 15 minutes and extracted in a microwave (CEM, MDS 2100) for one hour at 130°C. Slurry samples of experiment O4 till O6 and P1 till P8 were extracted using Acetone/Water (4/1 w.w.) as extraction solution. Then the solution was also ultrasonified for 15 minutes whereafter they were mixed end over end for one hour at 20°C. All the extracted samples were centrifuged and the supernatant was used for the PAH analyses.

6.2.4.2 PAH analyses

The concentrations of 16 PAH selected by the Environmental Protection Agency (USA) (16 EPA-PAH) were determined in the sample extracts. The HPLC-system contained a GasTorr-103 degasser, a Gynotech 480 HPLC-pump, a Spark Holland Basic-Marathon autosampler and a Waters 991 photodiode array detector. The separation of the 16 EPA-PAH is achieved by using a HPLC column with a length of 250 mm and a diameter of 4.6 mm, filled with Vydac 5, a C18 reversed phase matrix. The column is eluted with a mixture of acetonitrile and degassed water. The composition of the mobile phase is a 50/50% (v/v) mixture of acetonitrile concentration and water and the column is eluted for 5 minutes. The acetonitrile content is linearly increased to 99% in 15 minutes and this solution used for 19 minutes. The flow rate is in all cases 1.0 ml/min. The 16 EPA-PAH are measured with a photodiode-array detector and identified in the chromatograms by manual comparison of the sample spectra with that of the 16 standard EPA-PAH. The reported PAH concentrations (mg/kg d.m.) are the sum of the 16

EPA-PAH.

6.2.4.3 PAH removal

The PAH concentration reduction of the material that was collected as Settled + Remains was calculated as PAH removal according to the following equation.

$$\text{PAH removal} = \frac{[\text{PAH}]_i - \dfrac{[\text{PAH}]_r \text{ x d.m.}_r + [\text{PAH}]_s \text{ x d.m.}_s}{\text{d.m.}_r + \text{d.m.}_s}}{[\text{PAH}]_i} \qquad \text{(v)}$$

Where [PAH] = PAH concentration (mg/kg d.m.), d.m. = dry matter (g), i = initial, r = Remains, s = Settled

6.3 Results and Discussion

6.3.1 Overschie Sediment

The Overschie sediment was tested with one step (O1 till O4) flotation experiments and two step (O5 and O6) flotation experiments. Experiments O1 till O3 were carried out with slurry A and experiments O4 till O6 with slurry B. The floatability of Petrol harbor sediment was only tested with one step flotation experiments (P1-P8) using slurry C.

Experiments O1 till O3 were tests to observe the optimum conditions for PAH removal at low SDS concentrations. The addition of collector, the flow of slurry and of DA were varied. These experiments were performed in duplicate. Experiment O4 (carried out in four-fold) was the screening test with slurry B. Experiment O5 was equivalent to O4, but the fraction Settled was used for a second flotation step in experiments O6a till O6c. Experiments O6 were carried out in duplicate.

The results of the Overschie flotation experiments are presented in table 6.2 and figures 6.1 (O1-O5) and 6.2 (O5-O6). Table 6.2 presents the average values of influent dry matter content, the average values of the dry matter content, organic matter content and PAH concentration of the three fractions (Froth, Settled and Remains), the average measured and calculated PAH concentration of the influent and the average PAH removal according equation (v).

Table 6.2 *Results of the Overschie flotation experiments*

Experiment	*O1*	*O2*	*O3*	*O4*	*O5*	*O6a*	*O6b*	*O6c*
d.m. influent	28	11	14	28	137	10	11	11
Flow (ml/min)								
Slurry	50	70	70	30	30	30	30	30
Dissolved air (DA)	90	90	140	90	90	90	90	90
Collector (µ l)								
Diesel	231	231	231	-	-	-	100	100
Montanol	-	231	231	-	-	-	-	100
Frother (mg/l DA)								
SDS	0.058	0.058	0.058	30	30	30	30	30
Dry matter (%)								
Froth	10	11	16	15	13	23	13	9
Settled	82	78	74	72	80	72	68	70
Remains	8	11	10	13	7	5	19	21
Organic matter (%)								
Froth	48	48	49	42	32	32	31	32
Settled	40	38	38	42	33	32	32	31
Remains	34	37	33	43	33	33	32	33
PAH (mg/kg d.m.)								
Froth	480 (40)	420 (10)	550 (70)	650 (160)	957	310 (80)	280 (4)	300 (10)
Settled	98 (18)	83 (3)	97 (30)	120 (20)	121	100 (5)	110 (2)	110 (4)
Remains	53 (26)	66 (14)	91 (7)	100 (30)	122	94 (4)	120 (20)	110 (6)
Influent measured *	172 (20)	172 (20)	172 (20)	240 (10)	240 (10)	120 (1)	140 (0)	140 (2)
Influent calculated**	130 (9)	117 (8)	170 (17)	200 (40)	229	150 (10)	140 (3)	130 (2)
PAH removal (%)***	45 (8)	53 (2)	44 (16)	51 (8)	50	17 (5)	19 (4)	24 (2)

* From O1 till O5 the influent concentration (171.5) is measurements in the buffer slurry A. At O5 and O6 the influent is measured in each influent sample, taken from slurry B.

** The concentration of the influent is recalculated from the concentrations and dry mass of the 3 fractions; froth, fines and remains.

*** The PAH is calculated as described in formula v

For O1 till O3 the dry matter of the influent varied. This was caused by the low density (5-10% m/m) of the basic slurry and therefore, the exact amount of dry matter was difficult to calculate.

For all the experiments (O1-O6) the deviation from the average was around 5% for the dry matter percentages and around 2% for the organic matter percentages. The deviation from the average for the PAH concentrations is presented between brackets.

For experiments O1 till O5 the PAH concentration of the influent was measured in the basic hydrocyclone slurry. The PAH concentrations of the influent of O6a till O6c were measured in the influent slurries. The overall PAH concentration in the fractions Froth, Settled and Remains was calculated, “influent calculated”, and compared with the influent PAH concentration, “influent measured”, to obtain insight in the reliability of the experiment.

The results of the experiments O1 till O3 show that the dry matter that remained in the mixing compartment was around 10% in all these experiments. The Froth fraction was around 10%

for O1 and O2 and around 16% for O3. The relatively large dry matter concentration in O3 is reflected in the relatively low dry matter content of the Settled fraction. For O3 this percentage is 74% and in O1 and O2 this amount was slightly higher (82 and 78%, respectively). The dry matter results of O1 and O2 suggest that the influence of Montanol is small. The influence of the DA flow is most pronounced. A higher DA flow results in a higher percentage dry matter in the Froth. The effect of a low slurry flow is also not very pronounced.

The organic matter of the Froth (48-49%) was around 10% higher than that of the Settled fraction (38-40%) in O1 till O3. The organic matter percentage of Remains was except for O2 around 5% lower than that in Settled. The enrichment in organic matter in the Froth shows that the organic fraction is selectively recovered and this could suggest that the PAH concentration in the froth is higher than in the Remains or Settled fraction.

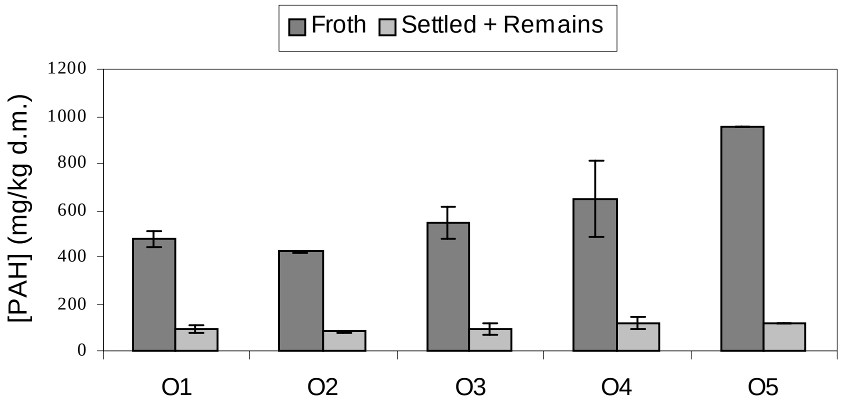


Fig 6.1 *PAH concentrations of Froth and Settled + Remains fractions in experiments (O1-O5)*

The results of the PAH analyses are presented in table 6.2 and highlighted in figure 6.1. Because the fractions Remains and Settled should be reusable, the overall PAH concentration in Settled + Remains fractions is plotted in fig 6.1. It is clear that there is a selective flotation of PAH. The PAH concentration in Froth is 4 to 6 times higher than the average concentration in the Settled + Remains (81-95 mg/kg d.m.). Regarding the Froth fractions the flotation result was optimum in O3 with Diesel and Montanol as collector plus a high DA/slurry flow ratio. Based on the PAH concentration in Settled + Remains, O2 with a lower DA flow gives the best remediation result. The average PAH removal, based on PAH concentration in Settled + Remains is for O2 53%, for O1 45% and O3 44%. Because the PAH balance of O3 is better (calculated and measured influent concentrations are almost similar) the results of O3 seem to be most reliable.

The PAH concentration of the Settled + Remains is in all the experiments (O1-O3) lower than the PAH concentration of the particle size fraction below 32 µm. This suggests that not only large particles are floated but also the particles below 32 µm.

A general problem with experiments O1, O2 and O3 was the bad quality of the froth. Although the airbubbles obtained from the dissolved air were of sufficient small size, the resulting froth was brittle and a lot of water had to be removed from the top to retain all the floated material. Therefore, in further experiments a higher SDS concentration of 30 µl/l DA has been used. As SDS can also act as collector, a high ratio of the DA and slurry flow was considered to be more important than the addition of an of an additional collector. The concentration of 30 µl SDS/l DA was the minimum concentration at which a stable froth was obtained. The DA-/slurry flow ratio was set to 3 with a DA flow of 90 ml/min and a slurry flow of 30 ml/min.

The results of experiment O4 show similar characteristics as the ones obtained in the previous experiments. Most of the material (72%) was carried out of the mixing zone but settled in the sedimentation zone. The Froth fraction (15%) is comparable to that in O3, but the Remains (13%) contained a little more material. The PAH concentration in Froth (650 mg/kg dm.) was again around 6 times higher than that in Remains + Settled, these results are also shown in fig 6.1. The PAH removal (51%) was relatively high and similar to that in O2. This confirms the assumption that the PAH containing particles could be selectively be floated from the Overschie sludge with SDS as frother. However, it is remarkable that the organic matter content of the three fractions is the same. This might be caused by the different basic slurry (B) which could be of different composition than slurry A. It is also possible that the stable froth and the fact that water removal at point E was not necessary, have caused that the organic matter fraction is no longer collected in the Froth fraction. The non-selectivity of the flotation with respect to organic matter is also observed in experiments O5 and O6.

In the experiment O5 the conditions of O4 are repeated with a larger volume of influent. The results are also incorporated in fig 6.1. The behavior is similar to that of O4 but some differences occur. Especially, the smaller amount of Remains and the higher amount of Settled, plus the higher PAH concentration in the Froth fraction should be noticed. These differences could be caused by the more continuous character of this flotation. Start up problems are more important in O4 than in O5 and could lead to more material in the Remains.

The second step flotation experiments of O6 show that from the Settled fraction of O5 another fraction of material could be floated. Without collector (O6a) the Froth contained a relatively high percentage of dry matter (23%). With Diesel (O6b) as collector only 13% was collected in the Froth and with Diesel and Montanol (O6c) as “collectors” this is even further reduced to 9%. The low percentages of dry material in Froth are reflected in the relatively high percentages Remains (O6b, 19%) an (O6c, 21%).

From these results it might be concluded that the addition of small amounts of the “collectors” Diesel and Montanol caused a low particle-bubble attachment efficiency instead of improving it. Additional experiments with 100 times larger amounts of agents (results not presented) showed that more material could be floated with these “collectors”, however, the PAH removal could not be increased.

The PAH removal of the second step flotation was around 20%. The variation of the removal percentages do not allow conclusions about the role of Diesel and Montanol. The PAH removal in O6b and O6c is mainly higher because the measured PAH influent concentration of O6b and O6c was slightly higher. On the other hand the PAH concentration in Settled and Remains is lowest in O6a suggesting again that addition of Diesel and Montanol is not enhancing the flotation efficiency.

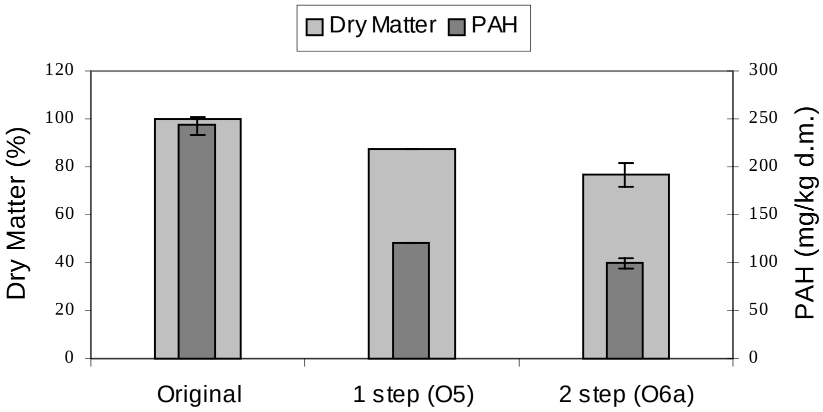


Fig 6.2 *[PAH] and [dry matter] of Settled + Remainsin the 2 step flotation experiment without collector*

The results of the first (O5) and the second (O6a) flotation step are summarized in fig 6.2. To this order the average dry matter content and the average PAH concentrations in Settled + Remains are calculated. The dry matter percentage of the second step is calculated with respect to dry matter amount of the original sludge. Also the PAH concentration of the original sludge is presented. Figure 6.2 clearly shows the good PAH removal of the first step and the poor PAH removal of the second step. Probably most hydrophobic PAH material is already floated in the first step. However, to fulfill the legally required limits for reuse it might be necessary to float a second time.

6.3.2 Petrol Harbor

Preliminary tests with the Petrol Harbor sludge showed that the frother SDS in combination with Diesel, Montanol and Aerophine as collector was incapable to treat this sludge. Merely 1% of the material could be floated and no PAH removal was observed. Most probably both the particles of the Petrol Harbor are negatively charged so that SDS, which creates negatively charged bubbles, act as depressor.

Table 6.3 Results of the Petrol Harbor flotation experiments

Experiment	*P1*	*P2*	*P3*	*P4*	*P5*	*P6*	*P7*	*P8*
d.m. influent (g)	32	37	38	38	40	40	35	39
Flow (ml/min)								
Slurry	30	30	30	30	30	30	30	30
Dissolved air (DA)	90	90	90	90	90	90	90	90
Collector (µl)								
Aerophine	-	-	42	42	-	-	-	-
Diesel	-	-	-	-	-	-	18.5	18.5
Frother (µl/l DA)								
Aerofroth	17	90	17	90	-	-	-	-
Montanol	-	-	-	-	8.0	38	8.0	38
Dry matter (%)								
Froth	54	69	67	71	57	63	50	67
Settled	39	26	28	24	38	31	41	27
Remains	7	5	5	5	5	6	9	6
Organic matter (%)								
Froth	20	21	22	21	23	22	23	21
Settled	16	16	16	15	17	16	18	15
Remains	16	13	13	10	14	12	16	10
PAH (mg/kg d.m.)								
Froth	2870 (70)	2370 (210)	2090 (30)	2070 (20)	2650 (280)	2200 (210)	2240 (170)	2120 (20)
Settled	1460 (50)	1180 (30)	1010 (20)	740 (130)	1120 (130)	1090 (430)	1210 (60)	690 (6)
Remains	670 (53)	630 (52)	570 (100)	310 (80)	920 (130)	570 (1)	980 (60)	440 (60)
Influent measured *	1990 (270)	1890 (160)	1650 (10)	1680 (30)	1560 (20)	1910 (330)	1580 (10)	1494 (30)
Influent calculated**	2160 (100)	1980 (200)	1710 (40)	1670 (70)	1960 (50)	1770 (260)	1710 (160)	1640 (50)
PAH removal (%)***	32 (7)	42 (3)	43 (3)	60 (5)	30 (7)	49 (11)	26 (3)	57 (0)

* The influent is measured at each influent sample, taken from slurry C.

** The concentration of the influent is recalculated from the concentrations and dry mass of the 3 fractions; froth, fines and remains.

*** The PAH is calculated as described in formula v.

In table 6.3 the results of the Petrol Harbor sludge experiments with Montanol and Aerofroth as frother (P1-P8) are presented. Montanol can not only be used as collector, but also as frother because it is a complex mixture of higher alcohols and esters with frothing activity. In experiments P1 till P4 Aerofroth was used as frother and in P3 and P4 also Aerophine was added as collector. In experiments P5 till P8 Montanol was used as frother. In P7 and P8 a further addition of Diesel as collector was applied.

Average values like in table 6.2 of the influent dry matter content, of the dry matter content, organic matter content and PAH concentration of the three fractions (Froth, Settled and Remains) are quoted, together with the measured and calculated PAH concentration of the influent and the average PAH removal ratio calculated with equation v.

The PAH concentration was measured separately for all the influent slurries. Table 6.3 shows that only for P5 a substantial difference exists between the calculated and measured PAH. For all the other experiments both concentrations were similar which suggest a good reliability of the experiments. For all the experiments (P1-P8) the deviation from the average was around 5% for the dry matter percentages and around 2% for the organic matter percentages. The deviation from the average for the PAH values is presented between brackets.

Remarkable for all the experiments (P1-P8) was the large amount of material collected in Froth (54-72%). Therefore, the Settled fraction (24-39%) was much smaller than with the Overschie sludge, and also less material was present in the Remains (5-9%). Increasing the amount of Aerofroth or adding Aerophine (P2 till P4) increased the amount of material in the Froth (67-71%) compared to only a low amount of Aerofroth in P1 (54%). Also the a higher concentration of Montanol (P6 and P8) leaded to high percentages dry matter in the froth (63-67%) compared to a low Montanol concentration in P5, P7 (57, 50%)

The organic matter percentages of P1 till P8 show that in the Froth (~22%) the organic matter content was mostly around 6% higher than in the Settled fraction (16%). The organic matter content of the Remains was often a few percent lower than in the Settled fraction, only in P1 it equals the organic matter percentage of the Settled fraction. The high percentage organic matter in Froth showed that the organic fraction is selectively floated from the Petrol harbor sludge.

The PAH concentrations in the Froth were about twice as high as those in the fraction Settled and 3 to 5 times higher than those in the Remains. The PAH concentration in both Settled and Remains was lower than that in the influent. These results are summarized in fig 6.3 where the average PAH concentration of the Settled + Remains are plotted together with the PAH concentration of the Froth and the influent (average values).

For the experiments with Aerofroth the lower PAH concentrations of P2 till P4 in both Froth and Settled + Remains reflect that in these experiments more material was floated than in P1. Because the flotation was not "highly" selective, the PAH concentrations in those Froth fractions is lower as also more material with a low PAH concentration is floated. However, there is still a certain selectivity which results in a lower PAH concentration of the Settled + Remains.

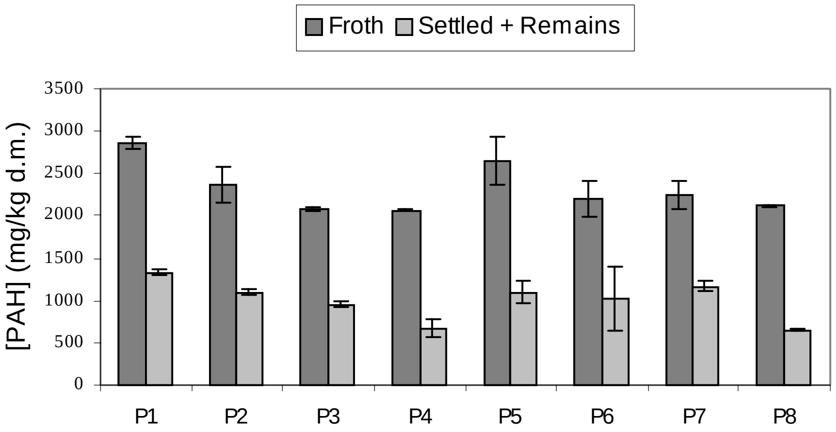


Fig 6.3 *PAH concentrations of Froth and Settled + Remains fractions in experiments (P1-P8).*

For the experiments with Montanol (P5 till P8) the relatively low dry matter content of Froth in P5 is reflected in a relatively high PAH concentration, but this does not hold for P7. Also with Montanol only a moderate selectivity is observed.

The lower concentration of PAH in the Settled + Remains could also been seen in the much lighter (brown) color of these samples compared to the darker (black) color of the Froth. However, in all the experiments with Petrol Harbor sediment the efficiency is insufficient for a one step flotation process, because the PAH concentrations in Settled + Remains were still far too high for reuse.

The moderate selectivity is also reflected in the PAH removal in Petrol Harbor sludge. With small amounts of Aerofroth or Montanol the removal is about 30%. The PAH removal was enhanced by adding larger amounts of Aerofroth (42%), and a further addition of Aerophine (60%). Increasing the amount of Montanol also increased the PAH removal (to 49%) and addition of Diesel further improved it to 57%.

Because the selectivity of the first step is low and the collected amount in the Froth is large, second step flotation experiments with Settled fractions were not carried out.

The results show that the flotation efficiency is different for both sludges (Overschie and Petrol harbor). Probably the relatively larger amount of small particles in slurry (C), the different composition of the sediment and the dissimilar origin of the PAH contamination make the separation of PAH containing particles less successful in the Petrol harbor sludge.

6.3.3 Soot Organic Matter

Finally, for the experiments O1-O3 the soot organic matter contents of the various fractions are compared with the PAH concentrations in these fractions in fig 6.5.

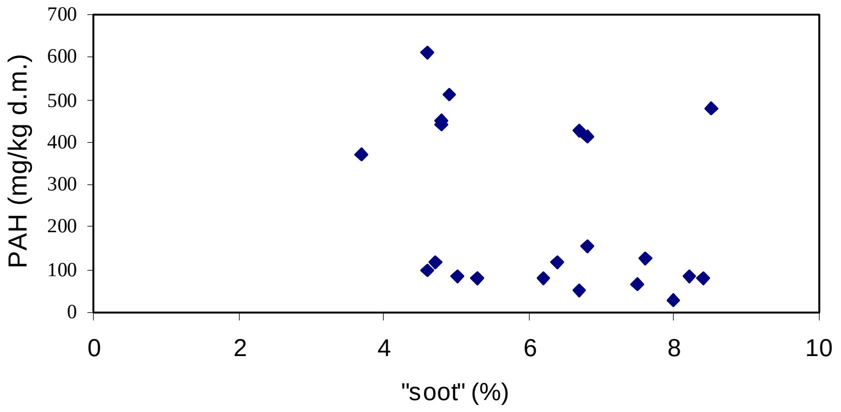


Fig 6.4 *Relation between Soot and PAH of all the samples in experiments (O1-O3)*

The graph shows that there is no simple correlation between the of Overschie fractions and the soot content. Hence, in this case the complicated PAH analysis can not be replaced with simple soot measurement. The correlation between the soot carbon content and PAH concentration in depth of sediment (associated with fossil fuel combustion) found by Gustafsson (Gustafsson et al. 1997) is not applicable for Overschie sediment, at least not at this micro-scale within the same sediment layer.

6.4 Conclusions

PAH containing particles can be selectively floated from even the finest fraction of dredged sediment from Overschie (Rotterdam) and the Petrol Harbor (Amsterdam).

For Overschie sludge, SDS is an appropriate frother. Generally around 13% of material was collected in the Froth and the PAH concentration in the Froth was around 4 to 8 times higher than the concentration in the Settled or Remains. The "collectors" Diesel and Montanol do not improve the flotation efficiency. Best results were thus obtained without collector. In one step, the PAH concentration in the Settled + Remains could be reduced with 50%. An extra 20 % reduction could be obtained in a second step flotation.

Petrol Harbor sludge flotation in the presence of SDS resulted in hardly 1% of dry material in the Froth fraction and SDS was therefore not an appropriate frother. With the alcoholic frothers Aerofroth and Montanol around 50% of material was floated. The flotation was not highly selective and the PAH concentration in the Froth was around 2 times higher than in Settled and 3-5 times higher than those in the Remains. The overall PAH removal is less good than in the case of Overschie sludge.

Also organic matter can be, depending on the basic slurry and sediment, selectively separated by dissolved air flotation.

Comparison of the soot content in the fractions with their PAH concentration revealed that for Overschie sediment the complicated PAH analysis can not be replaced with simple soot measurements.

7

General Discussion

7.1 Introduction

The main aim of the work described in this thesis is to selectively separate small particles by flotation. The research is mainly focussed on the remediation of fine fractions of PAH contaminated soil or sediment. In this chapter the functionality of the flotation device, the PAH removal efficiency of the remediation, the effect of flotation agents and the characterization of the sludge is broadly discussed.

7.2 Flotation Device

Small particles are an easy target to be transported into the froth through entrainment with the water flow or physical trapment by rising bubbles. These phenomena of entrainment and entrapment predominantly hinder successful selective separation of fine particles by flotation, because large amounts of undesirable hydrophilic particles will contaminate the froth.

In this research a new approach regarding selective flotation was introduced which might minimize the phenomena of entrapment and entrainment and therefore optimize the separation efficiency.

Common devices for ore and coal flotation use relatively large bubbles and turbulent flow regions dominate the reactors. Even in pneumatic column or Jameson flotation cells which are commonly regarded as devices which can handle fine particles, bubbles are generally larger than 500 µm. Bubbles used in flotation processes for wastewater treatment are mostly much smaller (10-100 µm). These smaller bubbles are often created by the use of dissolved air (DA). In this research DA was used, not to float all the particles like in waste water treatment, but for the selective separation of hydrophobic from hydrophilic particles. Several laboratory scale columns have been tested. Firstly a column was used with an extended tilted part behind the mixing zone (fig 3.2). The tilted part should enhance sedimentation and increase the separation efficiency. With this device hydrophilic particles in the range of 20-125 µm and hydrophobic particles in the range of 20-500 µm were separated. Approximately 2.5 % of the total mass consisted hydrophobic, PAH containing, soot particles. The other 97.5 % contained hydrophilic, non PAH containing, silica particles. From the high PAH removal in, and large amount of, the tailings, it was concluded that the recovery of soot particles was high whereas entrainment and entrapment of silica particles was minimized in this flotation device.

Using this column for even smaller particles would probably result in accumulation of these particles in the column. Therefore, in the second device the mixing and sedimentation zone were separated by a baffle that should prevent settled particles to fall back in the mixing zone of the reactor (fig 5.1). There is thus no accumulation of fine particles in the column. The separation of mixing and sedimentation compartment also creates an active counter current sedimentation flow which improves the settling velocity even more. This counter current flotation device showed to be an excellent device to selectively separate particles hydrophobic particles (MT-OX) of around 4 µm from hydrophilic particles (silica) of 2-25 µm. Grades (eq. iii) as high as 98.1% show that entrainment and entrapment is negligible even for the very small particles used.

Overall it can be concluded that the idea of using dissolved air as small bubble source together with a sedimentation zone, creates a flotation reactor that is capable of separating even the smallest particles without entrainment and entrapment. For other problems stemming from the flotation of fine particles, like excessive adsorption of reagents are of course not tackled by this different flotation approach.

The columns investigated were on laboratory scale. For the development of a more practical column the idea presented in figure 7.1 might be useful.

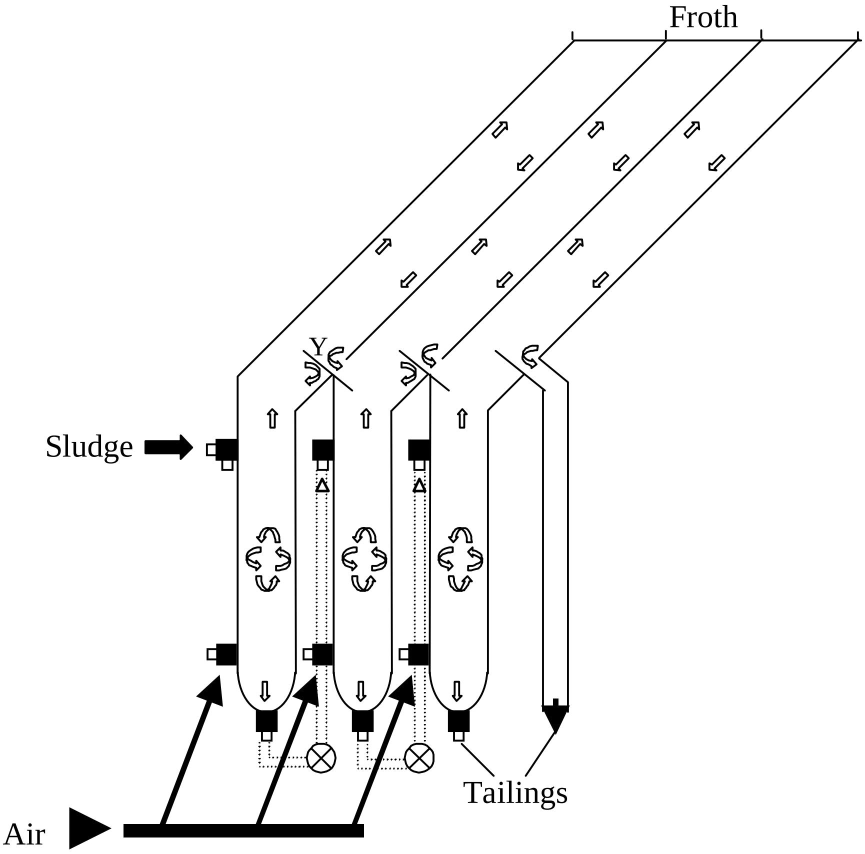


Fig 7.1 *Possible scale up of the counter-current sedimentation flotation device*

The baffle Y is extended so that the air inserted in the sedimentation zone does not float into the first compartment. Also several cells could be used separately or in succession. A problem that could occur with the use of dissolved air is the large amounts of water that has to be used in the process. Creating bubbles by electrolyte flotation is recommended to tackle this problem. Next to that the recovery rates are expected to be low because of the combination of as well small particles as slow rising dissolved air bubbles. The flotation device is therefore, probably better equipped to separate high value small particles or powders than bulk amounts of low value material as contaminated soils and sediment. However, it has clearly been shown that there is no obstacle to remediate even the smallest particle size fraction of contaminated soil or sediment as long as the contamination is present in hydrophobic particles and the remaining fraction of clean hydrophilic particles.

7.3 Remediation of PAH Contaminated Soil and Sediment

The fine fractions of soil and also sediment are difficult to treat by the conventional ex-situ techniques. Microbiologically, not all the contaminants are degradable and often rest concentrations are too high for reuse. Soil washing is also difficult because physical properties of contaminant and clean particles are often insignificant in the smaller particle range. In this research it has been shown that for polluted soil and sediment with the contamination in the hydrophobic part of the soil or sediment, flotation is an ideal solution.

The experiments with the smallest particle size fraction of classificated contaminated sludge (chapter 3) showed that the average PAH removal was around 85 % and under optimal conditions as high as 95%. The average PAH concentration in the remaining tailings was around 4 mg/kg d.m. and under optimum conditions even as low as 1.4 mg/kg d.m. The dry matter content of 98 % of the total mass of the tailings resulted in a large “reusable” fraction. If the tailings can be used is of course dependable on the law. Dutch PAH remediation policy is based upon the 10 VROM PAH (chapter 1) and not on the 16 EPA PAH. Because the flotation of PAH was non-specific in relation to the different PAH molecules, in all the experiments 10 VROM PAH can be estimated by multiplying with 10/16. For the PAH concentration of 1.4 mg/kg d.m. it means that the 10 VROM PAH concentration was 0.88 mg/kg d.m. which is under the target value of 1 mg/kg d.m. (see table 1.1).

When floating dredged sediment (Petrol Harbor and Overschie) in the particle range of 45-90 µm it was shown that the PAH contamination in the sludge, like the PAH concentration in the classificated sludge, was present in the hydrophobic fraction (chapter 4). Around 85 % of PAH could be removed from both sludges. Under optimal conditions the remaining tailings contain 92 % and 83 % of the total mass for Overschie and Petrol Harbor sludge, respectively. For Overschie the PAH concentration was reduced from 24 mg/kg d.m. to 3.6 mg/kg d.m. In regard to the Dutch standards this is from 15 mg/kg d.m. (10 VROM-PAH) to 2.25 mg/kg d.m. (10 VROM-PAH). This low PAH concentration, almost similar to the target value (see table 1.2), together with the relative high organic matter content suggested that the tailings of Overschie can be regarded as clean. For Petrol Harbor sludge with a much higher initial PAH concentration (1035 mg/kg d.m.) the 85 % removal resulted in a PAH concentration of the tailings of 148 mg/kg d.m (92.5 mg/kg d.m. 10 VROM PAH), which is still above the intervention value.

Floating the finest fractions of Overschie and Petrol Harbor did result in lower efficiencies (chapter 6) than obtained with the fractions (45-90 µm) of those sludges. For Overschie the flotation efficiency was with a PAH removal of 50 % and a tailing of 80%, still acceptable. The resulting PAH concentration in the tailings of Overschie was around 120 mg/kg d.m. (75 mg/kg d.m. 10 VROM PAH) for a one step flotation experiment and around 100 mg/kg d.m. (62.5 mg/kg d.m. 10 VROM PAH) for a second step flotation experiment. Intervention values for sediment with more than 30% organic matter (as this Overschie fraction) are 120 mg/kg d.m.. Flotation thus makes spreading, of the heavily contaminated smallest particle size fraction of Overschie sediment from, forbidden to allowed in exceptional cases (see table 1.3). For the finest fraction of the Petrol Harbor sludge PAH removal was also around 50 % but also around 50 % of the material was floated into the froth. The final concentration of PAH in the tailings was around 1000 mg/kg d.m. and thus far above the intervention value.

The evidence in chapter 5, that the counter current sedimentation flotation column used was capable of separating particles between 2 and 20 µm, suggest that in the case of the smallest particle size fraction of Petrol Harbor sludge clean and contaminant particles are not present as assumed. The high amount of oil in Petrol harbor sludge is likely spread over the smallest particles. This makes all the particles fairly hydrophobic and easily floatable. Also the clay present in the sludge could decrease the flotation efficiency dramatically (Arnold et al. 1986). For example clay could coat the hydrophilic particles which make them easily floatable when oil is attach to the clay.

Furthermore, it should be noted that removal efficiencies obtained are all for the restricted particle size fractions floated. Together with the other fractions of the soil or sediment, final concentrations can be much lower and reuse of the total fraction might still be possible.

Remediation of PAH contaminated soil or sediment will mostly result in the removal of soot- or tar-like particles which are hardly biodegradable because of the strong attachment of the PAH in these particles (Jonker et al. 2000). Next to that, like mentioned before, the remediation of PAH contaminated soil by flotation is non-specific on behalf of different PAH molecules. This means that also larger PAH molecules, which are hardly biodegradable (Agteren et al. 1998), are removed. The removal by flotation of the hardly bio-available PAH in soot particles as well as the removal of large amounts of difficult degradable large PAH molecules make the combination of flotation followed by biological remediation promising. The resulting PAH contamination in the tailings is lower and more diffusely spread over the matrix thus much better bio-available. It would therefore be very likely that biological treatment of the tailings can decrease the PAH contamination dramatically as already shown by (Klein et al. 1995).

Because of the different flotation approach and the smaller particle sizes used in this research and the different characteristics of all the soils and sediments, there has been made no comparison with other results done in the field of remediation by flotation as ascribed in chapter (2.7)

In general when the contamination is present in hydrophobic fraction and the other fraction exist out of clean hydrophilic particles, there is no limitation on behalf of the separation of these particles by flotation. The flotation reactors could succeed other classification processes, but can also be applied a single (mobile) remediation unit.

A good knowledge of the composition of the soil or sediment is recommended. Mostly the history of the contamination will expose important information. For PAH contamination especially, the contamination caused by deposition of soot particles will be more easy to treat by flotation than PAH contamination brought about by coal-tar spills. Finally like wheeler mentioned (Wheeler et al. 1987) will no recommendation or characterization replace actual testing. The flotation device in this research provide a practical quick tool to perform those tests.

7.4 Flotation Agents

It is common to enhance flotation by addition of for example collectors and frothers (chapter 2). Also in this research several helping agents are used to improve the flotation efficiency. It appeared that the effect of agents was not uniform over all the fractions. An improvement of the flotation efficiency of sludge x by agent a could lead to a decrease of efficiency of sludge y by that same agent.

For an efficient flotation of classificated sludge (chapter 3), addition of flotation agents was necessary. Screening test showed that Diesel (collector) + Montanol (frother/promotor) and Aerophine (collector) + Aerofroth (frother) are appropriate flotation agents. The activity of the Diesel and Montanol was further increased by emulsification. The excellent possibilities to improve the flotation efficiency with a combination of Diesel and Montanol was confirmed in the semi-continuous flotation experiments.

The experiments with dredged sediment of 45-90 µm (chapter 4) showed that the flotation efficiency could not be improved by a flotation agent. Montanol, Diesel, a combination of them and Aerophine + Aerofroth all decreased especially the selectivity of the flotation. The removal efficiency was often not or negatively influenced by the flotation agents.

The flotation process with smaller particle size fractions of dredged sediment in chapter 6 required a froth and thus a frother. For Overschie the anionic surfactant SDS appeared to be a functional frother, but for Petrol Harbor sludge an alcoholic frother like Aerofroth Montanol was needed. Most probably the particles in Petrol Harbor sludge were more weathered and therefore more negatively charged and thus didn’t have an affinity with the negatively charged SDS-bubbles. The flotation efficiency of the smallest particle size fractions of Overschie could not be improved by the addition of a collector. For Petrol Harbor the PAH removal could be increased with increased frother concentrations and addition of the collectors Aerophine or Diesel. However, the improving PAH removal was annulled by the lower selectivity of those tests.

The different concentrations used for the soil and sediment used are summarized in table 7.1

Table 7.1 Amounts of reagents used for the different soil and sediment fractions

	BSN	Overschie (45-90 µm)	Petrol Harbor (45-90 µm)	Overschie (<32 µm)	Petrol Harbor (<32 µm)
SDS (mg/l DA)	~	-	-	-	30
Aerofroth (µl/l DA)	-	-	-	-	17 / 90
Montanol (µ/l DA)	-	-	-	-	8 /38
Aerofroth (ml/kg)	-	14	14	-	-
Montanol (ml/kg)	3	8	8	10	-
Aerophine (ml/kg)	-	7	7	-	1
Diesel (ml/kg)	3	8	8	10	0.5

~ = Aliquots

- = not applied

/ = both amounts are used

Reagents used in coal flotation are around 500 mg/kg d.m. for oil and 125 mg/kg d.m. or 10 mg/l water, for frothers (Aplan et al. 1987; Arnold 1999; Firth 1999). Amounts used in this research are, except for the frother dose per liter, 10 to 150 times smaller. On first sight this might be strange but regarding the fact that the coal (organic matter) part in our slurry is much lower than in coal flotation make lower frother and collector amounts explicable.

From the screening tests with BSN sludge was concluded that concentrations as low as 3 mg/kg could be sufficient which was confirmed by the excellent flotation efficiency in the semi-continuous experiments. From this concentration the amounts for the relatively smaller particle size fraction 45-90 µm (larger surface area) and higher organic matter content were increased approximately 3 times. Because the negative effect of these amounts on the selectivity, the amounts were not dramatically raised for the smallest particle size fractions of sediment. In contrary the amounts were considerably decreased for the Petrol Harbor sludge when noticed that larger amounts had again a negative effect on the selectivity of the flotation of the finest fraction of Overschie sediment.

The flotation agents can be classified into several groups (chapter 2.4). However, this does not mean that an agent only can have one kind of activity. SDS for example is next to a frother also a collector. Also Montanol can be used for several purposes. Because of the alcoholic groups it has a frothing activity and is used for that in the flotation experiments with MT-OX + silica (chapter 5) and the smallest particle size fraction of Patrol Harbor sludge (chapter 6.3.2). But like mentioned by laskowski (Laskowski 1992) it can also be used as promotor to facilitate the adsorption of diesel to a particle as carried out with BSN, Overschie (45-90/ <32) and Petrol Harbor (45-90). Next to that, to see the separate effect, Montanol is also used as the collector in the 45-90 µm fractions of Overschie and Petrol Harbor sludge.

In general the results in this research show that flotation agents can improve the removal of PAH containing soot particles from a sandy soil sludge by flotation. When floating smaller particle size fractions as in the contaminated sediments, the effect of the collector was mostly negative. Suggested is therefore, that to successfully float fine fractions of contaminated sediment, the contaminated fraction should be naturally floatable and only a frother should be used. Frothers should be added with the DA solution.

Apart from the use of different frothers, the flotation efficiency might be improved by altering the pH of the slurry (not performed in this study). Most coal flotation plants run best at pH 7 (Aplan 1999), but PAH contaminated sludge might need another pH.

7.5 Characterization and PAH analysis

Contact angles have showed to be a good indication for the floatability of the analyzed particles. Larger contact angles corresponded with better floatability (chapter 3 and 4). Also when the differences in contact angle between particles became smaller the separation efficiency became less. However, the enhancement of the flotation results cannot be explained by changes in the contact angles only.

For the smallest particle size fraction (chapter 6), no contact angle studies were carried out. This was because it appeared to be very difficult to isolate different particles by using characterization techniques as, upstream columns or high density polytungstate solutions.

Throughout the research it can be conclude that fast and adequate results were difficult because of the laborious PAH analysis. It was very difficult to get a stable and robust PAH analyzing method. Often results changed significantly for on first hand similar soil or sediment samples. Partly this can be described to the strong heterogeneity of the soil and sediment, but the winded PAH analysis were definitely not helpful. Therefore, it was investigated if the PAH analysis could be changed by more simple measurement methods which gave a simple fast and reliable interpretation of the flotation efficiency.

For the 45-90 µm fractions of the sediments used, the organic matter content was as expected high in fractions with a relatively high PAH concentration. The flotation efficiency could therefore be estimated by the organic matter content in the fractions. For the smallest particle size fraction of PAH contaminated sediment this relation was not found. Organic matter was relatively much less or not selectively floated in the smallest particle size fractions. For these results the organic matter contents could thus not be used for an indication of the PAH removal which did occur in these experiments. Also the “soot” content analyzed (6.3.3) did not show a simple correlation with the PAH content in the fractions.

7.6 Concluding Remarks

The research has shown that the use of using dissolved air as small bubble source together with a sedimentation zone, creates a flotation reactor that is capable of separating even the smallest particles whilst minimizing the entrainment and entrapment. For contaminated soil it means that when the contamination is present in a hydrophobic fraction and the other fractions consist clean hydrophilic particles, there is no limitation for the separation of these particles by flotation.

The remediation of a sandy soil sludge contaminated with PAH was very successful and PAH removal could be further increased with flotation agents as Diesel and Montanol. The fraction of 45-90 µm of PAH contaminated dredged sediment from Overschie and the Petrol Harbor was also successfully treated with the flotation process used in this research. The flotation remediation efficiency was less for the smallest fractions (<32 µm) of these sediments, but PAH was still selectively removed.

The counter current flotation sedimentation cell is a practical tool to perform a quick laboratory test to investigate if contaminated soil or sediment could be remediated by flotation. Next to that, on basis of the laboratory experiments a prototype reactor could be developed to remediate even the smallest fractions of contaminated soil and sediment in practice. The flotation reactor could succeed other classification processes, but could also be applied a single (mobile) remediation step. Moreover, this new developed flotation process might even be more useful to selectively float higher value particles or powders in other industrial fields.

8

Summary

Samenvatting

8.1 Contaminated Soil and Sediment

As described in chapter 1, are polluted soils and sediments a threat for a sustainable environment. The polluting components, like Polycyclic Aromatic Hydrocarbons (PAH), are toxic and carcinogenic. Therefore, pollution of soil and sediment is of great concern to modern society. It is their duty to remediate contaminated soil and sediment and it is a necessity to prevent new spills, which are the origin of soil and sediment contamination.

Therefore, the Dutch government is spending millions of guilders a year for the urgent clean up of thousands of contaminated sites. Also millions of guilders will be spent on the remediation of the millions of tons of contaminated sediment that have to be dredged.

Several remediation techniques are on hand. Of them, soil washing (fig. 1.2) is the most common technique when dealing with excavated soil. This process uses physical and chemical particle properties to separate contaminated particles from the clean sandy soil. In general, firstly larger contaminants are removed, whereafter the soil or sediment is transformed into a slurry and classification techniques as hydrocyclones (fig. 1.3) and spirals follow. This mostly results in a clean sand fraction and several contaminated fractions, as the fines fraction. The fines fraction can for example be polluted with PAH containing tar- or soot particles. When treating soil and sediment with large amounts of small particles, the fines fraction will be relatively large and further treatment will be necessary. Flotation is a promising technique for this further treatment. Flotation techniques are broadly used in the mining industry for the upgrading of coal and ore, but also for the remediation of larger fractions of polluted soil.

The properties of the remediation of fine fractions of PAH contaminated soil and sediment by flotation is studied in this research.

8.2 Theory of Flotation

Chapter 2 deals with the theory of flotation. The principle of flotation is based on the capture of particles by bubbles and the collection of them in a froth layer. The process of selective flotation is graphically presented in figure 2.1: were hydrophilic particles settle and hydrophobic particles attach to air bubbles and float into the froth. For successful treatment of contaminated soil and sediment by flotation, the pollution has to be present in hydrophobic particles whereas the clean particles are hydrophilic.

The capture of particles by bubbles is on of the central processes in froth flotation. For an efficient capture particle and bubble must undergo a close encounter, governed by the hydrodynamics of the reactor. When attachment occurs and the overall attractive forces involved overcome detachment forces, the aggregate of bubble and particle is stable and the particle can float to the froth. The overall hydrophobicity of a particle can be measured by the contact angle (fig 2.5). In general, the larger the contact angle of the particle the better the flotation recovery.

Successful selective flotation of fine particles, as with contaminated soil and sediment, is hindered by entrapment and entrainment. These phenomena will carry a lot of undesired (hydrophilic) particles into the froth and therefore, decrease the selectivity. When using a special flotation design which uses for example smaller air bubbles, these phenomena might be decreased. An elegant way to create those small bubbles is the use of Dissolved Air (DA) as common in wastewater treatment.

Flotation efficiency can be enhanced by the use of helping agents like collectors, promoters and frothers. Collectors are agents that render the hydrophobicity to the particles. Frothers are surface-active molecules and provide a larger air-water interface (froth) to ensure that a floated particle will not fall back into the pulp. Promoters are used to enhance the attachment of a collector to the desired particle. The helping agents used for PAH contaminated soil are mostly derived from coal flotation, because the flotation of the contaminated soot/tar particles resembles to some degree to the flotation of coal.

8.3 Flotation of Contaminated Classificated Sludge

In chapter 3 is described how the froth flotation technique was applied to clean a sandy soil sludge contaminated with soot particles containing a large amount of PAH. To obtain insight into the flotation process, contact angles on soot pellets and silica plates were determined in both the absence and presence of several collectors and the results were compared with the flotation recovery of soot (90-200 µm) and silica (90-200 µm) from suspensions of the pure materials using a modified Hallimond tube. Aerophine, dodecylpyridinium chloride and three different oils were used as collectors. Adding a collector increased the contact angles on soot particles from 89^o to at least 100^o and increased the flotation recovery from 56% to 100%. However, the contact angle and the flotation recovery of silica are also enhanced under optimal conditions for soot flotation.

A semi-continuous dissolved air flotation apparatus (fig 3.2) was used for the practical flotation experiments. The contaminated sludge fraction contained silica particles of 20 to 125 µm and soot particles of 20 to 500 µm. The best flotation results were obtained when a combination of emulsified diesel oil as collector and emulsified Montanol (a mixture of higher alcohols) as frother was used. Under optimal conditions 95% of the PAH were removed and concentrated in only 2.5% of the total mass of the sludge.

8.4 Flotation of Very Fine Particles

In chapter 5 a new laboratory flotation system (fig 5.1) for the selective separation of small particles was designed and tested. The device contains an active counter current sedimentation that should prevent entrainment of the fine hydrophilic particles. The cell was used to selectively float fine particles in the size range of 2-25 µm. To create small bubbles Dissolved Air (DA) was used.

The study is linked to the problems that fine particles create by cleaning contaminated soils and sediments. Therefore, small silica and small oxidized carbon black (MT-OX) particles were used as model system. Three different frothers, Sodium Dodecylsulfate (SDS), Aerofroth and Montanol were applied to obtain a stable froth.

The results showed that the equipment works excellent to separate the fine MT-OX particles from the small silica particles. Especially with Aerofroth as frother, the Grade of the flotation experiments was extremely high (98.1%). The MT-OX Recovery was best with SDS (74.6%). The new flotation design provides a promising method for the remediation of contaminated sediments and soils. Next to that it offers an interesting option to separate fine particles and powders in other industrial applications.

8.5 Flotation of Contaminated Sediment

Besides the research on contaminated soil, also the applicability of dissolved air flotation to remediate PAH contaminated sediments of “Overschie” (Rotterdam) and “Petrol Harbor” (Amsterdam) is studied. Firstly the fractions of 45-90 µm are investigated. Several flotation reagents (Diesel Fuel, Montanol, Aerophine and Aerofroth) were applied to enhance the flotation efficiency. The physical chemical characteristics of the different particles in the presence of surfactants are investigated by contact angle measurements.

In the absence of reagents a one step batch flotation experiment removes around 85% of PAH from both sludges. The remaining tailings contain 92% and 83% of the total mass for the Overschie and the Petrol Harbor sludge, respectively. When reagents are added the efficiency of the process decreases. The remaining tailings contain only 80 to 60% of the total mass, whereas the PAH removal is not substantially enhanced and in some experiments even dramatically reduced.

After the successful treatment of the 45-90 µm fractions. The smallest fractions (<32 µm) of Overschie and Petrol harbor sediment were remediated by selective flotation. Therefore, the new laboratory device (fig 5.1) as presented in chapter 5 was used. Like with the fractions of 45-90 µm several flotation agents were tested to enhance the flotation efficiency.

For Overschie sludge the best results were obtained without collector or promoter and SDS as frother. The PAH concentration in the Froth was up to 8 times higher than that in the fractions collected as Settled or Remains. The collected amount of dry matter in Froth was around 13%. With a two step flotation, the PAH concentration of the “re-usable” Settled + Remains fraction was reduced from 240 mg/kg d.m. to 99 mg/kg d.m.

For Petrol Harbor sludge the best results were obtained with the alcoholic frothers Aerofroth or Montanol again without collector or promoter. The flotation was less selective than with Overschie sediment. Around 50% of dry matter was collected in Froth and the PAH concentration in the Froth was around 2 times higher than in the Settled fraction and 3-5 times higher than in the fraction Remains.

8.6 Conclusion

The research has shown that the use of using dissolved air as small bubble source together with a sedimentation zone, creates a flotation reactor that is capable of separating even the smallest particles with minimizing the entrainment and entrapment. For contaminated soil it means that when the contamination is present in hydrophobic fraction and the other fraction exist out of clean hydrophilic particles, there is no technical limitation on behalf of the separation of these particles by flotation.

8.1 Algemene Inleiding

Zoals beschreven in hoofdstuk 1 vormt vervuilde grond en sediment een grote bedreiging voor een gezond en duurzaam milieu. Vele verontreinigingen, als Polycyclische Aromatische Koolwaterstoffen (PAK), zijn namelijk toxisch en/of carcinogeen. Het is de plicht van de moderne samenleving om verontreinigde grond en sediment schoon te maken en tevens om te voorkomen dat er nieuwe bronnen ontstaan, die bodem of sediment kunnen vervuilen.

De Nederlandse overheid spendeert daarom miljoenen guldens per jaar om de meest urgente vervuilde locaties te saneren. Tevens zullen er in de toekomst miljoenen guldens worden uitgegeven aan de reiniging van verontreinigde baggerspecie.

Er zijn verschillende manieren om vervuilde grond te saneren. Voor afgegraven grond is de meest gebruikte techniek die van de natte-deeltjesreiniging (fig. 1.2). Dit proces gebruikt fysische en chemische eigenschappen om verontreinigde deeltjes van schone te scheiden (wassen). In het algemeen worden eerst de grovere deeltjes verwijderd. Daarna wordt de grond of het sediment getransformeerd in een slurrie waarna classificatietechnieken zoals hydrocyclonen (fig.1.3) en spiralen volgen. Veelal resulteert dit in een schone zandfractie en verscheidene vervuilde fracties, zoals de fijne fractie (fines) die nog vervuild kan zijn met bijvoorbeeld PAK-houdende teer- of roetdeeltjes.

Wanneer grond of sediment wordt behandeld met een grote hoeveelheid aan kleine deeltjes zal de fines-fractie relatief erg groot zijn en is verdere behandeling van deze fines gewenst. Een mogelijke behandelingsmethode is flotatie van de fines. De techniek van flotatie is niet nieuw en wordt al uitgebreid toegepast in de mijnbouw voor de verrijking van erts en kool, maar ook voor de reiniging van grovere fracties van verontreinigde grond.

In dit proefschrift is onderzocht of ook de fijne fractie van met PAK verontreinigde grond en sediment te reinigen is middels flotatie.

8.2 Flotatietheorie

In hoofdstuk 2 is de flotatietheorie behandeld. Het principe van flotatie is gebaseerd op de hechting van belletjes aan deeltjes en het opvangen van de deeltjes in een schuimlaag. Het proces van selectieve flotatie is schematisch weergegeven in figuur 2.1: hydrofiele deeltjes bezinken en hydrofobe deeltjes hechten aan luchtbellen en floteren in het schuim. Logischerwijs dient voor een succesvolle reiniging van vervuilde grond en sediment middels flotatie de vervuiling aanwezig te zijn in de hydrofobe deeltjes terwijl de schone deeltjes hydrofiel zijn.

Een van de centrale processen in flotatie is de hechting van een deeltje aan een belletje. Een efficiënte hechting kan alleen plaatsvinden bij een voldoende dichte nadering van deeltje tot belletje, hetgeen wordt gestuurd door de hydrodynamische krachten in de reactor. Wanneer hechting plaatsvindt en de overall attractieve krachten groter zijn dan de afstotende krachten zal het aggregaat van belletje en deeltje stabiel zijn en kan het deeltje floteren naar het schuim. De hydrofobiciteit van het deeltje kan worden bepaald aan de hand van de randhoek (fig. 2.5). In het algemeen geldt: hoe groter de randhoek van een deeltje hoe hydrofober en des te beter zal het floteren.

Succesvolle selectieve flotatie van kleine deeltjes, als bijvoorbeeld de flotatie van vervuilde grond en baggerspecie, wordt gehinderd door “entrapment” en “entrainment”. Deze verschijnselen voeren een hoop ongewenste (hydrofiele) deeltjes mee in het schuim en verminderen daardoor de selectiviteit van het proces. Deze verschijnselen kunnen worden verminderd met een speciale reactor waarin kleinere belletjes worden gebruikt. Een elegante methode om kleine belletjes te genereren is met behulp van opgeloste lucht. Dit proces van dissolved air (DA) flotatie wordt veel gebruikt in de afvalwaterzuivering.

De efficiëntie van de flotatie kan worden bevorderd door toevoeging van hulpchemicaliën, zoals “collectors”, “promotors” en “schuimers”. Collectors zijn chemicaliën die een deeltje hydrofoob maken. Schuimers (frothers) zijn oppervlakte-actieve stoffen die de oppervlaktespanning van het lucht/water-grensvlak vergroten, zodat gefloteerde deeltjes niet terugvallen in de reactor. Promotors (promoters) worden gebruikt om de hechting van een collector aan een deeltje te vergemakkelijken. De hulpchemicaliën die gebruikt worden bij de flotatie van met PAK vervuilde grond zijn afgeleid van de flotatie van kool, daar de flotatie van de verontreinigde roet/teer-deeltjes veel overeenkomsten heeft met de flotatie van kooldeeltjes.

8.3 Flotatie van Verontreinigde Grond

In hoofstuk 3 is beschreven hoe de flotatietechniek is gebruikt om een geclassificeerde zanderige grondslurrie, vervuild met roetdeeltjes die een grote hoeveelheid PAK bezitten, te reinigen middels flotatie. Om inzicht te krijgen in het flotatieproces zijn randhoeken bepaald aan roetpillen en silicaplaatjes met en zonder de aanwezigheid van verschillende collectors. Deze resultaten zijn vergeleken met de flotatieopbrengst van roet (90-200 µm) en silica (90-200 µm) uit een suspensie van puur materiaal. De flotatie-experimenten zijn gedaan met een Hallimond flotatiebuis. Aerophine, dodecylpyridiniumchloride en drie verschillende oliën zijn gebruikt als hulpchemicaliën. De toevoeging van een collector verhoogde de randhoek aan roetdeeltjes van 89^o tot ten minste 100^0 en verhoogde de flotatie-opbrengst van 56% naar 100%. Echter, bij deze optimale conditie voor roetflotatie werd ook de flotatie van silica sterk verhoogd.

De praktische flotatie-experimenten zijn gedaan met een semi-continue DA-flotatiebuis. De verontreinigde slibfractie bevatte silicadeeltjes in de range van 20 tot 125 µm en roetdeeltjes in de range van 20 tot 500 µm. De beste reinigingsresultaten zijn bereikt wanneer een combinatie van geëmulgeerde dieselolie als collector en geëmulgeerde Montanol (een mengsel van hogere alcoholen) als schuimer/promotor werd gebruikt. Bij optimale condities kon 95% van de PAK worden verwijderd en geconcentreerd in slechts 2,5% van de totale massa van het slib.

8.4 Flotatie van zeer kleine deeltjes

In hoofdstuk 5 is beschreven hoe een nieuwe flotatieopstelling (fig. 5.1) voor de selectieve flotatie van zeer kleine deeltjes is ontwikkeld en getest. Door de actieve tegenstroombezinking in de opstelling moet entrainment van zeer kleine deeltjes zo veel mogelijk worden voorkomen. De kolom is gebruikt om deeltjes in de orde van grootte 2-25 µm selectief van elkaar te scheiden middels flotatie. Opgeloste lucht is gebruikt om kleine belletjes te genereren.

Het onderzoek is gerelateerd aan de problemen die kleine deeltjes veroorzaken bij de reiniging van grond en baggerslib. Daarom is er gebruikt gemaakt van de modelstoffen silica en geoxideerde "carbon black” (MT-OX). Drie verschillende schuimers, Natrium Lauryl Sulfaat (SDS), Aerofroth en Montanol zijn gebruikt om een stabiele schuimlaag te creëren.

De resultaten lieten zien dat de ontwikkelde flotatieopstelling uitermate geschikt was om de kleine MT-OX-deeltjes te scheiden van de kleine silicadeeltjes. De grade (eq iii) was vooral erg hoog (98.1%) wanneer de schuimer Aerofroth werd gebruikt. De MT-OX-opbrengst (eq iv) was het hoogst (74.6%) met SDS als schuimer. Kortom de nieuwe flotatieopstelling is een veelbelovende methode voor de reiniging van verontreinigde grond en baggerslib. Bovendien is deze flotatieopstelling mogelijk ook geschikt voor scheiding van zeer kleine deeltjes en poeders in andere industriële toepassingen.

8.5 Flotatie van Verontreinigde Baggerspecie

Er is, behalve naar de mogelijkheid om verontreinigde grond te reinigen, ook onderzoek gedaan naar de reiniging van met PAK verontreinigde baggerspecie uit Overschie (Rotterdam) en de Petroleumhaven (Amsterdam) middels flotatie.

Allereerst is de fractie van 45-90 µm onderzocht. De flotaties zijn gedaan in een gemodificeerde Hallimond-buis. Hiervoor zijn verschillende hulpchemicaliën (Diesel, Montanol, Aerophine, Aerofroth en SDS) gebruikt. Aan de verschillende deeltjes van deze fracties zijn ook randhoekmetingen gedaan om de hydrofobiciteit te bepalen.

In de afwezigheid van hulpchemicaliën verwijdert een enkele flotatiestap ongeveer 85 % van de aanwezige PAK uit beide slibsoorten. De achterblijvende restslurries (tailings) bevatten respectievelijk 92% en 83% van de totale massa van het Overschie- en Petroleumhavenslib. De efficiëntie van het proces verminderde bij de toevoeging van hulpchemicaliën. Dit werd veroorzaakt doordat de achterblijvende tailings slechts 80% tot maar 60% van de totale massa bevatte en de PAK-verwijdering over het algemeen niet verhoogd werd en soms zelfs verlaagd.

Nadat met succes de 45-90 µm fracties waren gefloteerd werd ook getracht om de kleinste fracties (<32 µm) van Overschie- en Petroleumhavenslib selectief te floteren. Hiervoor werd de nieuwe flotatieopstelling (fig 5.1) gebruikt die is beschreven in hoofdstuk 5. Evenals in de voorgaande tests is ook ditmaal gebruik gemaakt van verschillende hulpchemicaliën om de efficiëntie van de flotatie te verhogen.

Voor het slib uit Overschie werden de beste resultaten verkregen zonder collector of promotor en met SDS als schuimer. De PAK-concentratie in de schuimfractie was tot 8 maal hoger dan in de overblijvende (Remains) of bezonken (Settled) fractie. De opgevangen hoeveelheid droge stof in de schuimfractie was ongeveer 13%. Met een tweetrapsflotatie werd de PAK-concentratie in de “herbruikbare” fracties Settled + Remains verlaagd van 240 mg/kg d.m. naar 99 mg/kg d.m..

Het beste resultaat met het Petroleumhavenslib werd eveneens verkregen zonder collector of promotor en deze keer met Aerofroth of Montanol als schuimer. De flotatie was minder selectief dan in het geval van Overschieslib. Ongeveer 50% van de totale droge stof werd opgevangen in het schuim en de PAK-concentratie ervan was ongeveer 2 keer zo hoog als in de Settled fractie en 3 tot 5 maal zo hoog als in de Remains fractie.

8.6 Conclusie

Het onderzoek heeft laten zien dat het gebruik van opgeloste lucht als bellengenerator, tezamen met een sedimentatiezone een flotatiereactor creëert die in staat is om zelfs de kleinste deeltjes selectief van elkaar te scheiden en de invloed van entrainment en entrapment te minimaliseren. Voor verontreinigde grond of baggerspecie betekent dit, dat wanneer de verontreiniging aanwezig is in de hydrofobe fractie en het hydrofiele gedeelte schoon is, er geen technische beperking is wat betreft de reiniging van het slib of de grond door middel van flotatie.

Agteren, M.H. van, S. Keuning and D.B. Janssen (1998). Handbook on biodegradation and biological treatment of hazardous organic compounds. Dordrecht, NL, Kluwer Academic Publishers.

AKWA (2001). Wet- en regelgeving binnen AKWA (factsheet 99.008), http://waterland.net/akwa/folder/fact/99008/index.htm.

Aplan, F.F. (1999). The historical development of coal flotation in the United States. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Colorado, Society for mining, mettalurgy, and exploration, Inc.

Aplan, F.F., S. Chandler and B.J. Arnold (1987). Reagents used in coal preparation. Chemical reagents in the mineral processing industry. D. Malhotra and W. F. Riggs. Littleton, Colorado, Society of Mining Engineers, Inc: 271-279.

Arnold, B.J. (1999). Rate and residence time studies applied to the operation of conventional coal froth flotation cells. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Colorado, Society for mining, mettalurgy, and exploration, Inc.

Arnold, B.J. and F.F. Aplan (1986). The effect of clay slimes on coal flotation part I: The nature of clay. Int. Journal of mineral processing 17(3/4).

Barbery, G. (1984). Engineering aspects of flotation in the mineral industry: Flotation machines, circuits and their simulation. The Scientific Basis of Flotation. K. J. Ives. The Hague, Martinus Nijhoff Publishers.

Bayraktar, I., A. Aslan and S. Ersayin (1998). Effects of primary slime and clay on selectivity of flotation of sub-volcanogenic, complex, polymetallic ores. Transactions of the institution of mining and metallurgy section c mineral processing and extractive metallurgy 107: C71-C76.

Bilz, E. and H. Weigel (1994). Schlammflotation für Hafenschlick. Umwelt 24: 445-447.

Bury, E., W. Broadbridge and A. Hutchinson (1920-21). Froth flotation as applied to the washing of industrial coal. Inst. Mining Engrs 60: 243-253.

Cassidy, M. B., H. A. E. Mulleneers, H. Lee and J. T. Trevors (1997). Mineralization of Pentachlorophenol in a Contaminated Soil By Pseudomonas Sp Ug30 Cells Encapsulated in Kappa Carrageenan. Journal of industrial microbiology and biotechnology 19(1): 43-48.

Cauwenberg, P. (1998). Speciation and behavior of transition metals in dredged material and their potential removal by flotation. Landbouwkundige en toegepaste biologische wetenschappen. Leuven, Katholieke Universiteit Leuven, PhD thesis**:** 161.

Cauwenberg, P. and A. Maes (1997). Influence of oxidation on sequential chemical extraction of dredged river sludge. International journal of environmental analytical chemistry 68 (1): 47-57.

Cauwenberg, P., F. Verdonckt and A. Maes (1998). Flotation as a remediation technique for heavily polluted dredged material. 1. A feasibility study. Science of the total environment 209 (2-3): 113-119.

Cauwenberg, P., F. Verdonckt and A. Maes (1998). Flotation as a remediation technique for heavily polluted dredged material. 2. Characterisation of flotated fractions. Science of the total environment 209 (2-3): 121-131.

Chang, H.N. (1947). Froth flotation of coal. Department of mineral engineering, Penn State University.

Chou, C. C., V. Ososkov, L. Zhang and P. Somasundaran (1998). Removal of nonvolatile hydrophobic compounds from artificially and naturally contaminated soils by column flotation. Journal of soil contamination 7 (5): 559-571.

Clifford, S. R. (1993). Removal of organic contamination from buffalo river sediment by froth flotation. Minerals and Metallurgical Processing november 1993: 195-199.

Cooper, H, M.C. Fuerstenau, C.C. Harris, M.C. Kuhn, J.D. Miller and R.F. Yap (1985). Flotation. SME mineral processing handbook. N. L. Weiss, SME.

Crawford, R. and J. Ralston (1988). The influence of particle size and contact angle in mineral flotation. International Journal of Mineral Processing 23: 1-24.

Crozier, R.D. and R.R. Klimpel (1989). Frothers: Plant Practice. Mineral Processing and Extractive Metallurgy review 5: 257-279.

CUR (1999). Aan het werk met het bouwstoffenbesluit. Gouda, VROM.

Cuypers, C. (2001). Bioavailability of PAH in soils and sediments: prediction of bioavailability and characterization of organic matter domains. Environmental Technology. Wageningen, PhD-thesis Wageningen University.

Cuypers, M. P., J. T. C. Grotenhuis and W. H. Rulkens (1998). Characterisation of PAH-contaminated sediments in a remediation perspective. Water science and technology 37(6-7)): 157-164.

Derjaguin, B.V. and S.S. Dukhin (1961). Theory of flotation of small bubbles and medium sized particles. Trans. Inst. Mining Met. 70(221).

Derjaguin, B.V. and S.S. Dukhin (1979). Kinetic theory of the flotation of fine particles. Thirteenth International Mineral Processing Congress, Warsaw, Elsevier Scientific Publishing company , Amsterdam.

Derjaguin, B.V and L.D. Landau (1941). Acta physicochem URRS 14(633).

Doelman, P. and G. Breedveld (1999). In situ versus on site practices. Bioremediation of contaminated soils: 539-557.

Dupre, V., M. Ponasse, Y. Aurelle and A. Secq (1998). Bubble formation by water release in nozzles **-** I. Mechanisms. Water research 32 (8): 2491-2497.

Eberius, E. and P. Ekke (1989). Verfahren zur dekontaminierung schlammartiger sediment. European pattent. Germany.

Edzwald, J. K. (1995). principles and applications of dissolved air flotation. wat. sci. tech. vol 31 No 3-4: 1-23.

Ende, K. van den and J Stronkhorst (2001). Onderzoek naar een nieuw beoordelingssysteem voor (zoute) bagger, http://waterland.net/akwa/anb1198/onderz1.htm.

Engbertsen, J.F.J. and Æ. de Groot (1988). Inleiding in de bio-organische chemie. Wageningen, Pudoc.

Evans, G.M., B.W. Attkinson and G. Jameson (1995). The Jameson Cell. Flotation Science and Engineering. K. A. Matis. New York, Marcel Dekker inc.

Eveson, G.F., S.G. Ward and F. Worthington (1957). Froth flotation of low rank coal II. A statistical investigation of six factors influencing froth flotation. J. Inst. fuel 30: 298-309.

Feenstra, L., J. Joziasse and M. Pruijn (1995). A standard method for characterizing contaminated soil and sediment for processing with particle separation techniques. Contaminated soil '95. W. J. v. d. Brink, R. Bosman and F. Arendt. Dordrecht, Kluwer Academic Publishers. volume II: 1123-1134.

Feng, D. and C. Aldrich (1999). Effect of particle size on flotation performance of complex sulphide ores. Minerals engineering 12(7)): 721-731.

Ferdinandy, M. (1999). Biologische technieken voor reiniging van baggerspecie, eindrapport. Lelystad, NL, POSW, Rijkswaterstaat.

Finch, J.A., A. Uribe-Salas and M. Xu (1995). Column Flotation. Flotation Science and Engineering. K. A. Matis. New York, Marcel Dekker inc.

Firth, B.A. (1999). Australian coal flotation practice. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Society for mining, mettalurgy, and exploration, Inc.

Fischer, S. (1982). Modellvorstellungen für die physikalischen-chemischen vorgänge in der flotationsstufe des deinking-prozesses. .

Fiscor, Steve (1992). Flotation Machines. Coal 97: 29-31 and 48.

Flynn, F. (1983). Precise air control key to efficient flotation cell deinking operation.

Fuerstenau, D.W. (1957). , Society of Mineral Engineering, 208, 1365.

Fuerstenau, D.W. and T.W. Healy (1972). Adsorptive bubble separation techniques. R. Lemlich. london, Academic Press: 91-131.

Fuerstenau, D.W., T.W. Healy and Somasundaran (1964). Trans. AIME 229: 321.

Fuerstenau, M.C. (1999). Froth flotation: the first ninety years. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Society for mining, mettalurgy, and exploration, Inc.

Gallios, G.P., K.A. Matis and Th Balabanidis, N. (1995). Dissolved-Air flotation of fine particles of salt-type minerals. Flotation Science and Engineering. K. A. Matis. New York, Marcel Dekker, inc.

Gillette, J. S., R. G. Luthy, S. J. Clemett and R. N. Zare (1999). Direct observation of polycyclic aromatic hydrocarbons on geosorbents at the subparticle scale. Environmental science and technology 33(8)): 1185-1192.

Gorree, M. (1995). Beschrijving en evaluatie van de normstelling voor PAK in baggerspecie. Leiden, CML.

Groen, K.P. (1999). Advies- en kenniscentrum waterbodems - AKWA. Bodem 2: 52-53.

Gustafsson, Örjan., Farnaz. Haghseta, Charmaine. Chan, John. Macfarlane and Philip. M. Gschwend (1997). Quantification of the dilute sedimentary soot phase: Implications for. Environ. Sci. Technol. 31: 203-209.

Haarhoff, J. and V. van Vuuren (1993). A south african design guide for dissolved air flotation. Pretoria, Republic of South Africa, Water research commission.

Habil, R., K. Tittel, K.O. Borchers and F. Nacken (1995). erfahrungen mit der entwässerung feinstkörniger rückstande aus einer bödenwaschanlage. Aufbereirung-Technik 36(8): 366-371.

Hadley, S., V. Choudhry, M. Mishra and M. Placha (1999). development and demonstration of fine coal cleaning circuit optimization. SME Annual Meeting.

Hansen, R.D. and R.R. Klimpel (1987). Coal Frothers. Chemical reagents in the mineral processing industry. D. Malhotra and W. F. Riggs. Littleton, Colorado, SME.

Heerema (1995). Flotatie en flocculatie voor M3, deel 2: Praktische aspecten. Delft, Delft University, faculty of mining.

Hemmings, C.E. (1980). An alternative viewpoint on flotation behaviour of ultrafine particles. Trans. Instn Min. Metall (Sect. C. Mineral Process. Extr. metall) 89: 113-120.

Hemmings, C.E. (1981). On the significance of flotation froth liquid lamella thickness. Trans. Instn Min. Metall (Sect. C. Mineral Process. Extr. metall) 90: 96-102.

Hendriksen, X (2000). personal communication, A.Hak contractor.

Henkens, Ch. H. (1994). Inleiding. Bodembescherming, handboek voor milieubeheer. F. A. M. d. Haan, C. H. Henkens and D. A. Zeilmaker. Alphen aan den Rijn, Samson H.D. Tjeenk willink bv.

Henner, P., M. Schiavon, V. Druelle and E. Lichtfouse (1999). Phytotoxicity of ancient gaswork soils. Effect of polyciclic aromatic hydrocarbons on plant germination. Org. Geochem. 30: 963-969.

Hiemenz, P.C. (1977). Priciples of colloid and Surface chemistry. New York, Marcel Dekker.

Hoek, C. van and D. Hartmann (2001). De vraagbaak voor bagger en bodem, Beslissingsondersteunend systeem voor natte deeltjesscheiding. Delft, NOVEM, http://t2000.novem.nl.

Hofstra, M.A. (1995). Remediation of contaminated soil. POSW. P. B. Roeters and G. N. M. Stokman. Zoetermeer, Hageman Verpakkers: 11-32.

Honaker, R.Q., A. Patwardhan, M.K. Mohanty and K.U. Bhaskar (1999). Fine coal cleaning using the Jameson Cell: the North American experience. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Society for mining, mettalurgy, and exploration, Inc.

Hussain, S. A., S. Demirci and G. Ozbayoglu (1996). Zeta Potential Measurements On Three Clays From Turkey and Effects of Clays On Coal Flotation. Journal of colloid and interface science 184(2): 535-541.

Ives, K. J. (1984). Scientific basis of flotation. The Hague, Martinus Nijhoff Publishers.

Ives, K.J. and H.J. Bernhardt (1995). Water Science and Technology. Oxford, Elsevier Science Ltd.

Jameson, G.J. (1984). Experimental techniques in flotation. Scientific basis of flotation. K. J. Ives. The Hague, Martinus Nijhoff Publishers.

Jameson, G.J. (1988). A new concept in flotation machine design. Min. Met. Process feb: 44-47.

Jawalapersad, N. (2001). personal communication. RIZA, Lelystad

Johnson, N.W., D.J. McKee and A.J. Lynch (1974). Flotation rates of non-sulphide minerals in chalcopyrite flotation processes. Trans. Amer. Inst. Min. Metall. Petrol. Engrs 256: 204-226.

Jones, M.J. and R. Oblatt (1984). Reagents in the minerals industry. Reagents in the minerals industry, Rome.

Jonker, C. and Smedes (2000). Environmental science and technology 34: 1620-1626.

Jowett, A. (1983). Particle size effects in coal flotation. Symposium on improving froth flotation of coal.

Kasi, M.P., F.O. Azzam and S. Lee (1993). Coal agloflotation and supercritical wet oxidation: Novel remediation techniques for ultra-cleaning of contaminated soils. Journal of Hazardous materials 35: 17-30.

Kirjavainen, V. M. (1996). Review and analysis of factors controlling the mechanical flotation of gangue minerals. International Journal of Mineral Processing 46(1-2): 21-34.

Kitchener, J.A. (1984). The froth flotation process: past, present and future-in brief. The scientific basis of flotation. K. J. Ives. The Hague, Martinus Nijhoff Publishers: 3-53.

Klein, J., F. Pfeifer, C Sinder and V. Mann (1995). Reinigung PAK-kontaminierter böden mit denm DMT-BIODYN-Verfahren. .

Koopal, L.K., T.P. Golub, A. de Keizer and M.P. Sidorova (1999). Colloids and Surfaces A:Physicochemical and Engineering aspects 151.

Kotterman, M.J.J. (1998). Polycyclic aromatic hydrocarbon degradation by the white rot fungus Bjerkandera sp. strain BOS55. Industrial Microbiology. Wageningen, PhD-thesis Wageningen University.

Langen, M. and B. Hamacher (1994). Prospects for separation heavy metals from contaminated. Aufbereitungs-Technik 35(1): 1-12.

Laskowski, J.S. and J.D. Miller (1984). New reagents in coal flotation. Reagents in the minerals industry, Rome, The intsitution of mining and metallurgy.

Laskowski, J. S. and J. Ralston (1992). Colloid chemistry in mineral Processing;. Amsterdam, Elsevier 428.

Leeson, A and B.C. Alleman (1999). Phytoremediation and innovative strategies for specialized remedial applications. Columbus, Ohio, Battelle Press.

Leja, J (1982). Surface chemistry of froth flotation. New York, PLenum Press.

Lovell, V.M. (1982). Industrial flotation reagents. Principles of flotation. R. P. King. Cape Town, Cape and Transvaal Printers (Pty) Ltd.

Mackenzie, J.M.W. (1970). Trans. AIME 247.

Meenan, G.F. (1999). Modern coal flotation practices. Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Society for Mining, Metallurgy, and Exploration, Inc. (SME).

Melik-Gaykazian, V.I., I.N. Plaksin and V.V. Voronchikhina (1967). Dokl. Akad. Nauk. SSSR 173.

Mischuk, N.A., L.K. Koopal and S.S. Dukhin (2001). Microflotation suppression and enhancement caused by particle/bubble elctrostatic interaction. Journal of colloid and interaces science 237: 208-223.

Mohanty, M. K. and R. Q. Honaker (1999). Performance optimization of Jameson flotation technology for fine coal cleaning. Minerals engineering 12 (4): 367-381.

Mohanty, M. K., R. Q. Honaker and B. Govindarajan (1999). Development of a characteristic flotation cleaning index for fine coal. International journal of mineral processing 55 (3): 231-243.

Mulleneers (2001). Selective separation of fine particles by a new flotation approach. Separation Science and Technology submitted.

Mulleneers, Huib., Suzan. Roubroeks, Harry. Bruning, Wim. Rulkens and Luuk. Koopal (2000). Flotation of PAH-contaminated dredged sludge. Surfactant-Based Separartions (science and technology). J. F. Scamehorn and F. H. Harwell. Washington, DC, America Chemical Society. ACS symposium series 740: 248-259.

Mulleneers, H. A. E., L. K. Koopal, G. C. C. Swinkels, H. Bruning and W. H. Rulkens (1999). Flotation of soot particles from a sandy soil sludge. Colloids and surfaces a physicochemical and engineering aspects 151 (1-2): 293-301.

Neesse, Th and H. Grohs (1991). Washing and classifying of contaminated soil. Aufbereitings-Techniek 32(2): 72-77.

Niewiadomski, M., J. Hupka, R. Bokotko and J. D. Miller (1999). Recovery of coke fines from fly ash by air sparged hydrocyclone flotation. Fuel 78 (2): 161-168.

Osborne, D. G. (1988). Flotation, agglomoration and selective flocculation. Coal preparation technology. London, Graham and Trotman Limited: 415-473.

Pearl, M. (1995). Review of potential techniques to overcome limitationscreated by fine particles during ex-situ soil separation. Abingdon, AEA Technology, National Environmental technology centre.

Pearl, M., G. Lejeune, B. Croft and P. Parsonage (1996). Investigation of Enhacement techniques for ex-situ soil separation processes, particularly with regard to fine particles. Abingdon, AEA Technology, National Environmental Technology Centre.

Peng, F. F. (1996). Surface energy and induction time of fine coals treated with various levels of dispersed collector and their correlation to flotation responses. Energy & Fuels 10 6 nov-dec: 1202-1207.

Plette, A.C.C. and J. Rienks (1999). Immobilisatietechnieken voor verontreinigde baggerspecie, Eindrapport. Lelystad, POSW, Rijkswaterstaat.

Ponasse, M., V. Dupre, Y. Aurelle and A. Secq (1998). Bubble formation by water release in nozzle - II. Influence of various parameters on bubble size. Water research 32 (8): 2498-2506.

Ralston, J. (1999). Controlled flotation processes: Prediction and manipulation of bubble-particle capture. Journal of the south african institute of mining and metallurgy 99 (1): 27-34.

Ralston, J., D. Fornasiero and R. Hayes (1999). Bubble-particle attachment and detachment in flotation. International journal of mineral processing 56 (1-4): 133-164.

Ralston, J. and G. Newcombe (1992). Static and dynamic contact angles. Ralston, J. J. S. Laskowski. Amsterdam, Elsevier: 173-203.

Ralston, O.C. and Wichmann (1922). The froth flotation of coal. Chem. and Met. Eng 16(11): 500-503.

Ramirez, J. A., A. Zinchenko, M. Loewenberg and R. H. Davis (1999). The flotation rates of fine spherical particles under Brownian and convective motion. Chemical engineering science 54 (2): 149-157.

RIZA (1998). Deel 31 Praktijkproef thermische verwerking van baggerspecie uit de petroleumhaven Amsterdam. Lelystad, RIZA.

Rubio, J. (1996). Modified Column Flotation of Mineral Particles. International journal of mineral processing 48(3-4): 183-196.

Rulkens, W.H. and H. Bruning (1995). Cean-up possibilities of contaminated soil by extraction and wet classification: effect of particle size, pollutant properties and physical state of the pullutants. Contaminated soil '95. W. J. v. d. Brink, R. Bosman and F. Arendt. Dordrecht, Kluwer Academic Publishers. volume II: 761-773.

Rulkens, W.H., H. Bruning, H.J. van Hasselt, J. Rienks, H.J. van Veen and J.P.M. Terlingen (1998). Design of a solvent extraction process for PAH-contaminated sediments: the WAU-acetone process. Water Science and Technology 37: 411-418.

Rulkens, W.H., T.A. Meeder and E.R. Soczo (1994). Saneringstechnieken voor verontreinigde landbodems. Bodembescherming, handboek voor milieubeheer. F. A. M. d. Haan, C. H. Henkens and D. A. Zeilmaker. Alphen aan den Rijn, Samson H.D. Tjeenk willink bv.

Rykaart, E.M. and J. Haarhoff (1995). Behaviour of air injection nozzles in dissolved air flotation. Wat. Sci. Tech. 31(3-4): 25-35.

Schulze, H.J. (1984). Physico chemical elementary processes in flotation, Analysis from point of view of colloid science. Amsterdam, Elsevier.

Schulze, H.J. (1993). Coagulation and flocculation, theory and applications. Surfactant science series. B. Dobias. New York, Marcel Dekker. 47.

Seitz, R.A. and S.K. Kawatra (1987). The role of nonpolar oils as flotation reagents. Chemical regants in the mineral processing industry. D. Malhotra and W. F. Riggs. Littleton, Colorado, Society of mining engineers, Inc: 171-179.

Seselj, A., J. Strazisar and B. Salopek (1997). Use of column flotation in the soil remediation process. IMPC, Aachen.

Shibata, J., S. Matsumoto, H. Yamamoto, E. Kusaka and Pradip (1996). Flotation separation of plastics using selective depressants. International Journal of Mineral Processing 48(3-4): 127-134.

Slims, R.C. and M.R. Overcash (1983). Fate of polynuclear aromatic compounds in soil -plant systems. Residue Reviews 88: 1-68.

Somasundaran, P., L Zhang, J. Zheng, V. Ososkov and C.C. Chou (2001). Removal of non-volatile hydrophobic compounds from soil by flotation. 1 Laboratory investigation using a mechanically agitated machine. Advances in Environmental Research 1(2).

Song, S. X., A. Lopez Valdivieso and Y. Q. Ding (1999). Effects of nonpolar oil on hydrophobic flocculation of hematite and rhodochrosite fines. Powder technology 101 (1): 73-80.

Stewart, J.W. (1932). Some experimental results with froth flotation on bituminous coal. Mineral Industries 2(3): 1-3.

Subrahmanyam, T. V., C. A. Prestidge and J. Ralston (1996). Contact angle and surface analysis studies of sphalerite particles. Minerals Engineering 9: 727-741.

Suedfeld, P. and R. A. Borrie (1999). Health and therapeutic applications of chamber and flotation restricted environmental stimulation therapy (REST). Psychology and health 14 (3): 545-566.

Tills, H.M.G.C. (1990). Fine particle flotation in a centrifugal force field. Chemische Proceskunde. Eindhoven, Universiteit Eindhoven.

Townsend, F. (1982). Factors influencing the the need for improved reagent systems for the flotation of coal. CIM Second technical conference on western Canadian coals.

Trahar, W.J. (1981). A rational interpretation of the role of particle size in flotation. International Journal of Mineral Processing 8: 289-327.

Trahar, W.J. and L.J. Warren (1976). The flotability of very fine particles - a review. International Journal of Mineral Processing 3: 103-131.

Ulberg, Z. (1997). Flotation Process For the Recovery of Metals and For the Biodecontamination of Waters and Soils Contaminated By the Chernobyl Accident. Research in microbiology 148(6): 522-523.

Varadaraj, Ramesh. (1994). Decontamination of hydrocarbon containing substrates (LAW100). United States Patent. USA, Exxon Research and Engineering Company.

Venghaus, T. and J. Werther (1998). Flotation as an additional process step for the washing of soils contaminated with heavy metals. Contaminated soil '98, Edinburgh, Thomas Telford.

Venghaus, T. and J. Werther (1998). Flotation of a zinc-contaminated soil. Advances in Environmental Research 2(1).

Vermeulen, J., S. van Dijk, T. Grotenhuis, J. Joziasse and W. Rulkens (2000). Accelerated physical ripening of PAH and oil contaminated sediment to distinguish critical steps in remediation. Contaminated Soil 2000, Leipzich, Thomas Telford.

Verweij, E.J.W. and G. Th Overbeek (1948). Theory of stability of lyophobic colloids, Elsevier.

Visschers, M.K. and K. Verschueren (1988). Teer en PAK-problematiek bij onderzoek van bodembeschermingsgevallen met teerachtige stoffen, VROM, staatuitgeverij 's-Gravenhage.

VROM (2000). Streefwaarden en interventiewaarden bodemsanering. Staatscourant 39.

VROM (2001). Het Nederlandse bodembeleid, http://www.minvrom.nl/minvrom/pagina.html.

VvAV (1997). Afvalverwerking in Nederland. Utrecht, Vereniging van afvalverwerkers.

VW (2000). Gewijzigde versie bijlage A: Normen 4e nota waterhuishouding. staatscourant 114.

Warren, L.J. (1984). Ultrafine particles in flotation. Principles of mineral flotation. M. H. Jones and J. T. Woodcock. Parkville, Victoria, Australia, The Australian Institute of mining and metallurgy. 40.

Weiss, N.L. (1985). SME Mineral Processing Handbook. Littleton, Society for Mining, Metallurgy, and Exploration, Inc.

Werther, J. and M. Wilichowski (1990). Investigation of the physical mechanisms involved in the purification of contaminated soils by washing processes. Contaminated Soil '90. Dordrecht (NL), Kluwer Academic Publishers. Vol.II: 907-921.

Wevers, H.H.A.G. and J. Lindenberg (1995). Remediation of contaminated soil. POSW. P. B. Roeters and G. N. M. Stokman. Zoetermeer, Hageman Verpakkers: 133-134.

Wheeler, T.A. (1995). Coal floats by itself - doesn't it? Reagents for better metallurgy, WITCO Corperation: 131-142.

Wheeler, Thomas. A. and Robert. O. Keys (1987). Factors influencing choice of coal flotation reagent. Chemical reagents in the mineral processing industry. D. Malhotra and W. F. Riggs. Littleton, Colorado, Society of mining engineers, Inc: 291-305.

Wilichowski, M. (1994). Aufbereitung mineralkontaminierter Böden durch bodenwäsche und flotation. Umwelttechnik. Aachen, PhD-thesis Technischen Universität Hamburg-Harburg.

Wilichowski, M., T. Venghaus and J. Werther (1998). Flotation as a process step in the treatment of soils contaminated with mineral oils. Environmental Technology 19(8): 801-810.

Wilichowski, M. und Werther J. (1995). Untersuchungen zur Einsetzbarkeit der Flotation bei der Wäsche Kontaminierter Böden. Chem. Ing. Tech;. 67 nr 6: 760-763.

Yoon, R. H. and L. Q. Mao (1996). Application of extended DLVO theory .4. Derivation of flotation rate equation from first principles. Journal of Colloid and Interface Science 181(2): 613-626.

Young, P. (1982). Flotation Machines. Mining Magazine January: 35-59.

Zabel, T. (1984). Flotation in water treatment. The scientific basis of flotation. K. J. Ives. The Hague, Marinus Nijhoff Publishers.

Zhang, L., P. Somasundaran, V. Ososkov and C. C. Chou (2001). Flotation of hydrophobic contaminants from soil. Colloids and surfaces a physicochemical and engineering aspects 177(2-3) Special Iss. SI): 235-246.

Zimmerman, R.E. (1948). Flotation. Coal Preparation, 2nd ed. D. R. Mitchell. New York, AIME: 570-587.

"Ik moet niet meer!"
en daarvoor wil ik de studenten Dale Rudrum, Martijn Smit, Suzan Roubroeks, Sander Boot, Harro de Vries, Bart van Gelder, Bart van der Mark en Joost Geraets van harte bedanken. Zonder jullie hulp was het nooit gelukt.
Ook wilde ik graag mijn (co)-promotoren Luuk Koopal, Harry Bruning en Wim Rulkens bedanken. Luuk, je kennis en enthousiasme hebben me altijd enorm gemotiveerd. Achteraf gezien had ik veel vaker langs moeten komen. Harry, bedankt voor je scherpe analyses en droge humor. Wim u ook bedankt.
Natuurlijk wil ik ook graag mijn directe collegae, Nico (ook voor de lay-out en pdf), Chiel, Jaap, Johan, Sybren, Michiel, Frank (ook voor je kennis van het ABN en het plat-Zeeuws), Gabor, Luc, Anneke en Dale (daar heb je hem weer) bedanken voor de gezelligheid. Sorry dat ik altijd zo nodig ieder spelletje wilde winnen. Daarnaast wilde ik nog eenieder bedanken die bewust en onbewust heeft bijgedragen aan dit onderzoek, met name Ilse, Johannes, Tim, Heleen, Liesbeth en uiteraard ook de werkplaats en de glasblazers.

Hier wilde ik het eigenlijk bij laten, maar na wat whisky's wilde ik het volgende toch nog even kwijt. Toen ik in september 1996 begon als aio waren enkele reacties uit mijn omgeving als volgt:
"Zou je niet gaan werken!", "Dat verdient toch niet?", "Ga je nu nog een groter afstudeervak doen?", "Jij aio?", en de topper van de afgelopen jaren "Hoelang moet je nog ?" (toen al).
Beste familie, vrienden, kennissen, collegae en onverwachte lezers. Zelden heb ik spijt gehad van mijn keuze (zeker nu het bijna afgelopen is) en ik heb me de afgelopen jaren prima vermaakt.

Huib Mulleneers werd geboren in 1971 te Didam. Na zijn studie milieuhygiëne, met als specialisatie milieutechnologie, is hij in september 1996 begonnen aan zijn promotieonderzoek, dat tot oktober 2001 geduurd heeft.

Cassidy, M.B., **Mulleneers, H.A.E**., Lee, H., Trevors, J.T.,(1997) Mineralization of Pentacholorophenol in a contaminated soil by *Pseudomonas sp UG30* cells encapsulated in k-carrageenan. Journal of Industrial Microbiology and Biotechnology 19 (1) 43-48

Mulleneers, H.A.E., Bruning, H., Koopal, L.K., Rulkens, W.H., (1997) Flotation and characterisation of contaminated sludge. Proceedings of International conference “Interfaces Against Pollution” Wageningen, The Netherlands

Mulleneers, H.A.E., Koopal, L.K., Bruning, H., Rulkens, W.H., (1998) Flotation of Harbor sludge. Proceedings of 215th American Chemical Society Meeting Dallas, TX, USA

Mulleneers, H.A.E., Bruning, H., Koopal, L.K., Rulkens, W.H., (1998) Treatment of contaminated soil and dredged sludge by an new flotation approach. Proceedings of the 6th International FZK/TNO Conference on Contaminated Soil, Edinburgh, UK

Mulleneers, H.A.E., Koopal, L.K., Swinkels, G.C.C., Bruning, H., Rulkens, W.H., (1999) Flotation of soot particles from a sandy soil sludge., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 151, 293-301

Mulleneers, H.A.E., Roubroeks, S., Bruning, H., Rulkens, W.H., Koopal, L.K., (2000) Flotation of PAH-contaminated dredged sludge. In: *Surfactant-Based separations*: Science an Technology (ACS symposium series, 740); J.F. Scamehorn, J.F. Harwell (eds); Oxford University Press: New York 248-259.

Mulleneers, H.A.E., Bruning, H., Koopal, L.K., Rulkens, W.H., (2000) Flotation of the fine fraction of contaminated dredged sediments. Proceedings of the Conference “flotation 2000” Adelaide, Australia

Mulleneers, H.A.E., Mark van der, B.C., Bruning, H., Koopal, L.K., Rulkens, W.H., (2000) Treatment of dredged sediments by a counter current flotation sedimentation technique. Proceedings of the 7th International FZK/TNO Conference on Contaminated Soil, Leipzich, Germany.

Mulleneers, H.A.E., Bruning, H., Rulkens, W.H., Koopal, L.K., (2001) Selective separation of fine particles by a new flotation approach., Separation Science and technology, (submitted)

Mulleneers, H.A.E., Mark van der, B.C., Geraets, J. Gelder, van B., Bruning, H., Rulkens, W.H., Koopal, L.K., (2001) Remediation of the finest fraction of dredged sediment by flotation, Environmental Technology (submitted).

Talent komt vanzelf wel bovendrijven.