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TECHNOLOGICAL PROSPECTION OF THE FLOTATION PROCESS APPLIED TO OILY-WATER TREATMENT

Raquel Santos Macedo

Master´s thesis presented to the Programa de Pós-graduação em Engenharia de Processos Químicos e Bioquímicos, from the Escola de Químicos of the Universidade Federal do Rio de Janeiro, as partial fulfillment of the requirements for the degree of Mestre em Engenharia de Processos Químicos e Bioquímicos.

Advisors: Prof. Ricardo de Andrade Medronho, PhD
Prof. Suzana Borschiver, D.Sc.

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“The meaning of life is that it is to be lived"
Bruce Lee

Abstract of the Master´s thesis presented to Programa em Engenharia de Processos Químicos e Bioquímicos - EQ/UFRJ, as partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

TECHNOLOGICAL PROSPECTION OF THE FLOTATION PROCESS APPLIED TO OILY-WATER TREATMENT

Raquel Santos Macedo
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Advisors: Ricardo de Andrade Medronho, PhD
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A technological prospection of the flotation process applied to the treatment of the oil containing wastewater by means of the analysis of scientific papers from Science Direct and Scopus databases and patents from the USPTO (American patent base) and INPI (Brazilian patent base) was carried out. The papers and patents were initially searched using keywords then reviewed manually to filter for the desired application. The method of analyses consisted of classification of the documents in taxonomies distributed over a Macro, Meso and Micro study. The macro evaluation comprised the time series from 2010 till part of 2017, and an investigation of the countries and affiliation/assignee of the documents. The Meso study comprised the process technique, apparatus type, sector of application and characteristic of the document contents corresponded to each group. Finally, a Micro analysis investigation was conducted over topics of interest.

The number of papers and patents oscillated through the last years. Countries as China, Brazil and US stood out with more contributions. The oil and gas industry was the main sector involved in the developments. The induced gas flotation was the process type with more incidence, and the compact flotation unit (CFU) was the model with more highlights considering both groups. A significant quantity of devices and studies related to rotational flow was found, which may indicate a trend on the usage of centrifugal force to improve the separation in this process. Moreover, there were developments related to additive/chemicals and monitoring tool such as control and instrumentation.

Key words: Flotation. Water treatment. Oily water. Produced water. Separation.

Resumo da Dissertação de Mestrado apresentada ao Programa em Engenharia de Processos Químicos e Bioquímicos da Escola de Química/UFRJ como parte dos requisitos necessários à obtenção do grau de Mestre em Ciências (M.Sc.)

PROSPECÇÃO TECNOLÓGICA DO PROCESSO DE FLOTAÇÃO APLICADO AO TRATAMENTO DE ÁGUA OLEOSA

Raquel Santos Macedo
Dezembro 2017

Orientadores: Prof. Ricardo de Andrade Medronho, PhD
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Uma prospecção tecnológica do processo de flotação aplicado ao tratamento e água contendo óleo residual através da análise de artigos científicos da base de dados do *Science Direct* e *Scopus* e patentes da base de patentes americana (USPTO) e brasileira (INPI) foi realizada neste trabalho. Os documentos foram inicialmente pesquisados utilizando palavras-chave e posteriormente revisados de forma a filtrar a aplicação desejada. O método de análise consistiu em classificar os documentos em taxonomias distribuídas entre Macro, Meso e Micro. A avaliação macro compreendeu a série histórica entre 2010 e parte de 2017 e foi uma investigação de países e organizações vinculadas ao documento. O estudo Meso compreende a técnica do processo, tipo de aparato, setor de aplicação e características do conteúdo do documento correspondente a casa grupo. Por fim, a análise Micro desenvolveu uma investigação detalhada sobre tópicos de interesse.

A quantidade de artigos e patentes oscilou nos últimos anos. Países como China, Brasil e Estados Unidos se sobressaíram com maiores contribuições. A indústria de óleo e gás foi o principal setor envolvido nos desenvolvimentos. A flotação por gás induzido foi o tipo de processo com maior incidência, e a unidade de flotação compacta (CFU) foi o modelo de equipamento de maior destaque considerando ambos grupos. Foram encontradas quantidades significativas de dispositivos e estudos relacionado a escoamento rotacional, o que pode indicar uma tendência da utilização da força centrífuga na melhoria da separação neste processo. Além disso, houveram desenvolvimentos relacionados a aditivos/químicos e ferramentas de monitoramento como controle e automação.

Palavras-chave: Flotação. Tratamento de água. Águas Oleosas. Água produzida. Separação.

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ACRONYM LIST

BTEX Benzene, toluene, ethylbenzene and xylene
CFU Compact flotation unit
CONAMA *Conselho nacional do meio ambiente* (Brazilian Environmental Council)
DAF Dissolved air flotation
DGF Dissolved gas flotation
EOR Enhancing oil recovery
FCSMC Cyclonic-static micro-bubble flotation column
IAF Induced air flotation
IGF Induced gas flotation
INPI *Instituto Nacional da Propriedade Industrial* (Brazilian patent base)
NEITEC *Núcleo de Estudos Industriais e Tecnológico*s (Technologic and Industrial Study Center)
O&G Oil and gas
PAHs Polycyclic aromatic hydrocarbons
PSC Primary separation cell
PW Produced water
R&D Research and development
TOG Total of oils and grease
TRP Technology roadmap
USPTO United States Patent and Trademark Office
USEPA United States Environmental Protection Agency
WIPO World Intellectual Property Organization

1. INTRODUCTION

In the oil and gas primary processing, the conventional processes to separate the phases (gas, oil, water and sands/sediments) are by gravity separation. Internally adjusted vessels provide proper flow conditions and residence time for the droplets to reach their rich phase. Subsequently, each primary separated phase stream passes through further separation process for appropriated polishing. The water phase, commonly referred as produced water (PW), may contain emulsified oil and very small particles, such as those of 10 micrometer and less in diameter, that do not rise according to Stokes' Law, and heavy oil that have similar density of the water – both challenges for separation (Atarah, 2011).

Produced water is the largest byproduct or waste stream associated with oil and gas production (Veil, et al., 2004). Its composition and properties vary greatly from location to location and even over time in the same well (Moosal, et al., 2002). The two most common destinations of this water are the reinjection in the well or its discharge into the environment (sea in case of offshore production). Both destinations require controlled concentration of contaminants, to avoid clogging of the well and to comply with governmental discharge restriction, respectively. The constituents of produced water that receive the most attention in both onshore and offshore operations are the oil and grease. Management of these contaminants presents challenges and costs to the operation (Veil, et al., 2004).

Proportion of oil:water varies through lifetime of the production field and can reach up to 1:10 (Atarah, 2011) for cases of mature fields. Water volumes tend to increase as the oil and gas field reaches maturity and is also affected by water injection for reservoir pressure maintenance. Produced water production volumes worldwide are in the order of 300 million barrels (50 million m^3) in daily bases with a rising curve (Ahmadun, et al., 2009). As large volumes of produced water are being discharged to open ocean stricter oil/grease discharge limits are enforced in oil and gas (O&G) sectors.

In addition to the O&G oily wastewater issue, increasing world population has been escalating waste effluents and became significant issue of environmental concern because of the toxicity of pollutants. According to the Global Risk Report of the World Economic Forum, clean water availability is part of the top five risks facing the world in the next decade (Wor16). As many countries face some degree of water stress, more than a billion people living in such locations are exposed. The increased uncertainty about future water availability, affected by water quality, underlines the importance of wastewater handling worldwide.

In order to avoid health and environmental issues caused by the raise in oily wastewater discharge, the oil concentration levels in wastewater effluent streams are stringently monitored by regulatory agencies in most parts of the world (Saththasivam, et al., 2016). The Brazilian and American agencies, respectively CONAMA (*Conselho Nacional do Meio Ambiente* - Brazilian Environmental Council) and USEPA (U.S. Environmental Protection Agency), stablish the maximum monthly average concentration of the total of oils and grease (TOG) in effluent disposal in the seabed is 29 mg/L (29 ppm) (CON) (Clark, et al., 2009). Onshore discharge limits can be even more rigorous due to lower dilution.

The treatment of oily wastewaters poses a huge challenge because of their heterogeneous composition and the large volumes generated by various industries. This oily wastewater can be treated through different physical, chemical, and biological methods. In case of the offshore platforms because of space constraints, compact physical and chemical systems are used. In facilities where footprint is not a major limitation, biological pretreatment of oily wastewater can be a cost-effective and environmental friendly method. However, most of the current technologies cannot remove small suspended oil particles and dissolved elements (Ahmadun, et al., 2009). One of the feasible, practical and established methods to remove oil contaminants from wastewater sources is by gas flotation.

In the flotation process, gas bubbles are injected in the influent compartment and flows through the medium where it can collide and attach with suspended particles. The working mechanism of gas flotation is primarily governed by the density differences between bubble-particle aggregate and the medium, in this case, water. The aggregates, which are lighter then water, floats to the surface and can be removed.

There are different devices that can be applied in flotation processes. Some facilities use tanks for batch processes, others choose column based continuous processes, or even apply centrifuge force for improving separation. Several alternatives for bubble generation are available in the market, and bubbles sizes may vary from millimeters down to nanometers. The process parameters are selected according to the type of effluent and its final application.

A wide range of parameters and devices can be applied to gas flotation and vast universe from science to the industry is related to the flotation process. Hydrodynamics of the medium, interfacial properties and droplets size distribution from both particles and bubble are important variables in flotation. Chemicals may help to improve performance. Apparatus features also contribute to process enhancements and the designs vary according to the desired application. Tools for better understanding and control the processes are applied in development centers, like process simulation. Flotation processes started in the XIX century in the mineral processing industry and undergone many improvements that nowadays make it possible to treat difficult to separate oil in water emulsions.

Due to its origin and intense use in the mineral area, developments in this industry were much more intense than in other areas. Challenges handling tricky solution and fluid properties and the need of additives, like for oil-water emulsions, demand innovation and R&D efforts in order to improve the process. A common issue among the experts are the vast unknown gaps and the need for optimization that demand effort from both researchers and practitioners as new techniques and theoretical approaches are used (Rawlins, 2011).

This background was the motivation for this work, which consists in analyzing the latest developments in gas flotation to come up with a comprehension of the latest developments and trends of this technology. The chosen method for this study is the technological prospection, which is a set of concepts and techniques applied to foresee the behavior of variables such as socio-economic, political, cultural and technological as well as the effects of their interactions (Borschiver, et al., 2016). Such evaluation is useful because it provides the main players, detects trending factors, identifies areas receiving more attention, highlights features/elements attracting more interest, investigates the relation between factors, and arises a development profile.

The objective of this work is, via technological prospection, to evaluate the gas flotation as a process to remove oil from oily wastewater. The chosen technique makes use of scientific papers and patents as base material of information. The goal by analyzing the content and profile of research studies and innovative intellectual properties is to obtain an overview of the current development scenario, estimate tendencies and supply valuable information to help institutions planning.

2. LITERATURE REVIEW

Flotation phenomena (also spelled floatation) is relative to the buoyancy of objects and this phenomenon can be explored by different science areas. In this study, the flotation process is related to the processing engineering method utilized for separation purposes.

The gas flotation process can be applied for a variety of purposes as ore beneficiation, drinking water purification and a vast type of waste processing. This work aims at the application of flotation in the treatment of oily wastewater. Oily water is a common waste stream in a range of industry, such as food, mineral, textile, shipping, petrochemical and oil and gas production. Moreover, oil is a common contaminant in municipal wastes whose volume rates rise with populations growth. Particular emphasis is given to produced water waste due to its volume proportions and significant impacts due to the O&G industry.

On the following items the processes key steps are described including the flotation types, the mechanism involved in the phenomena, apparatus design as well as supportive features. In addition, a brief explanation of effluents is given. Endmost, an overview of the technological prospection is presented.

2.1. Flotation process

Flotation can be spontaneous when the specific mass of particles to be eliminated is lower than that of water, or it can be artificially stimulated by setting up bubbles of gas onto the particles to be removed, giving them an average specific mass less than water (Scholz, 2006).

Flotation is a gravity controlled process driven by drag force. A gas is released in the system, it collides and attaches to the particles and form an aggregate/floc. Since the agglomerates have a lower density than the medium in which they are immersed, they rise to the surface where they are removed. The governing equation for the terminal velocity of bubble/drop under laminar flow conditions is predicted by Stoke’s Law, presented in eq. 1:

$$V_t = \frac{gD^2(\rho_{med} - \rho_{ag})}{18\mu_{med}} \quad \text{(Stoke´s law)} \qquad (1)$$

Where $\mathbf{V_t}$ is the upward terminal velocity of the aggregate; $\mathbf{g}$ is the gravitational acceleration; **D** is the diameter of the particle/aggregate; $\boldsymbol{\rho_{ag}}$ is the density of the aggregate; $\boldsymbol{\rho_{med}}$ and $\boldsymbol{\mu_{med}}$ are the density and viscosity of the continuous medium, respectively.

As can be seen from the Stokes equation, it states that the rise velocity is dependent on bubble/droplet diameter and density difference. The smaller is the oil droplets the slower is the rise velocity. Attaching gas to oil reduces its density, thereby increasing the diameter and density difference between the aggregate and water, in this manner producing a faster rise rate (Atarah, 2011).

The four key steps of a gas flotation system are summarized below (Wang, et al., 2010):

1. <u>Gas bubbles generation</u> – the bubble size and gas volume with respect to particle concentration are very important parameters for an efficient performance. Large bubbles and low gas volume generally leads to poor capture efficiency.
2. <u>Contact/collision between gas bubbles and particle</u> – frequent collision between gas bubbles and oil droplets is essential to promote the bubble-drop adhesion.
3. <u>Attachment of gas bubbles</u> – Establishing a strong adhesion between gas bubbles and oil droplets is important to generate the required flotation buoyancy force. Improper or weak attachment leads to poor oil–water separation efficiency.
4. <u>Rise of the bubble-particle aggregates to the concentrate phase</u>– process conditions should prevent detachments of the bubble-particle aggregates, so the flocs can flow upward through the medium in the device and reach the concentrate phase. Excessive physical disturbance can break up the aggregate.

These four steps are more detailed in the following items. The phenomena occurring on each of them are accounted for the calculation of the process efficiency – presented right afterwards, on item 2.2.

2.1.1. Bubble generation

Flotation is classified primarily based on the method of bubble formation, and its classification vary from author to author. Several specific groups can be labeled. In this work, it was decided to adopt the generic approach that is divided in the main types listed below and detailed subsequently (Eskin, et al., 2015)(Edzwald, et al., 2011)(Wang, et al., 2010)(Rubio, et al., 2002):

- Dissolved gas flotation - The gas is released from a supersaturated solution as a result of pressure reduction. In this case, very small gas bubbles are formed and rise to the surface.
- Induced (or dispersed) gas flotation - The gas is introduced directly in the waste stream by different methods. The bubble generation and/or dispersion will vary according to the feature like spargers, eductors, porous media, impellers, etc.
- Electroflotation - The bubbles are generated by electrolysis of the water. The electrolytic decomposition of water is with oxygen release on the anode, and hydrogen liberation on the cathode.

Table 1 presents some process parameters (Wang, et al., 2010)(Eskin, et al., 2015). The process characteristics vary among the flotation systems and are reported differently among authors, such as bubble size data presented in the table. The differences can be related to the substances, process conditions, experimental equipment, etc. Moreover, it shall be taken into consideration that the efficiency depends on the fluid characteristics and operational variables.

Table 1: Parameters from the main flotation systems (Wang, et al., 2010)(Eskin, et al., 2015).

Author	Parameter	Dissolved gas flotation	Induced gas flotation	Electro-flotation
Eskin, et al.	Efficiency (%)	60-75	Up to 92,5	Up to 90
	Average bubble diameter (µm)	20-200	500-6000	50-100
Wang, et al.	Average bubble diameter (µm)	75	170	100
	Bubbles rising velocity (cm/s)	0.2 (0.1)	3 (1.5)	1 (0.5)
	Number of bubbles /cm^3	$3,6x10^6$	$0,2x10^4$	10^6
	Bubbles surface area (cm^2/cm^3)	800	293	454

2.1.1.1. Dissolved gas flotation

In the dissolved gas flotation (DGF) gas saturation is obtained by pressurizing raw water or part of the (un)treated recycle wastewater stream in a pressure tank, or by means of a (appropriate) pump (generally 10% to 30% of the amount to be treated (Scholz, 2006)). Afterwards, the pressure is reduced to, as a rule, normal atmospheric pressure. The gas can also be saturated in water in atmospheric pressure and, in this case, vacuum should be applied in the flotation unit. The amount of gas released is small in such cases (Edzwald, et al., 2011). A DGF (dissolved gas flotation) system that uses air as gas is also called DAF (dissolved air flotation). Pressure differences of 4–5 bar are usually selected in a standard DGF system (Wang, et al., 2010). The amount of gas going into solution obeys Henry's Law, presented in eq. 2:

$$p = kC \quad \text{(Henry´s law)} \tag{2}$$

Where **p** is the partial pressure of the gas, **C** is the concentration of the gas dissolved in the solution, and **k** is the Henry's Law constant.

As per the equation, the amount of gas dissolved in solution and consequently the amount of gas released upon reduction of pressure are direct functions of the initial air pressure. The gas consumption for the case of water treatment by dissolved air flotation varies, on average, between 15 and 60 l/m^3 of water to be treated (Scholz, 2006).

In this way, important variables in the generation of gas bubbles are pressure difference between the gas saturation process stage and the flotation chamber, and the proportion of (recycled waste) water relative to the income waste stream. The type of nozzle, aerator or injector also affect average bubble dimension and its size distribution, as can be observed on Figure 1. Moreover, the interface tension is important since itis associated with the maximum size of stable bubbles and indicates when coalescence will occur (Wang, et al., 2010).

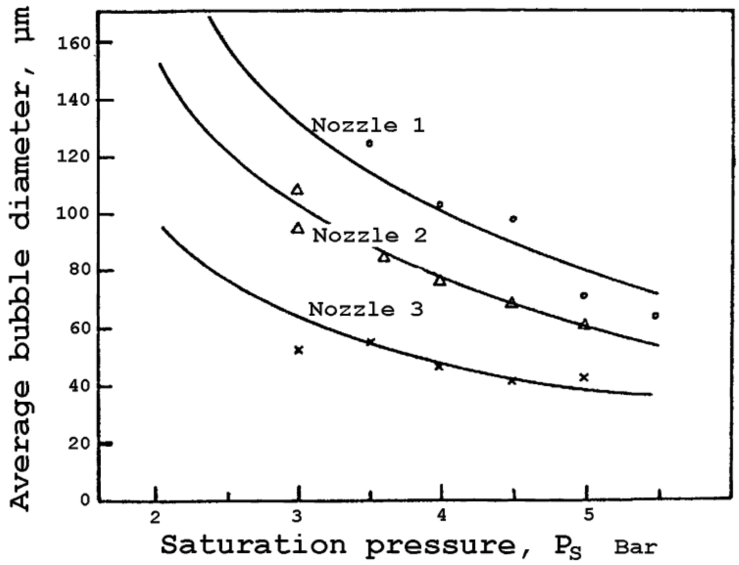


Figure 1: Bubble size as function of saturation pressure for different nozzles.
Source:(Wang, et al., 2010)

Air bubble formation in dissolved gas flotation

In the dissolved gas flotation, the air bubble formation is conceptually simplified to three consecutive steps: i) Nucleation, ii) Growth and iii) Coalescence.

The nucleus theory is a phenomenon where a gas coming out of a solution from a liquid will preferentially form a bubble on a finite nucleus, found, for instance, in solid surfaces. In case of contaminants/particles are present in the region of the depressurization they can serve as well as nucleation sites. In the absence of nucleation sites, bubbles form homogeneously on nucleation sites in the liquid phase. These nucleation sites in liquids are likely to be centers of liquid eddies that can be formed due to the turbulent depressurization within the nozzles. The pressure is lower in the centers of these eddies than in the surrounding water, bringing about the bubble arise. Therefore, the efficiency of bubble formation also depends on the intensity of turbulence created at the point of depressurization. Higher pressure pushes the water through the nozzle at higher velocity, leading to more nucleation sites. In terms of the conceptual bubble formation model, more nucleation sites should generate smaller bubbles (Edzwald, et al., 2011)(Atarah, 2011).

For the case of oily water treated with hydrocarbon gases, like natural gas, as the solubility of the gas in water is several orders of magnitude lower than in liquid hydrocarbon, most of the gas effervescing will come from the oil droplets. After the nucleation on the droplet, it will continue to grow as pressure drops. Eventually one bubble can contact other and coalesce (Rawlins, 2011). This mechanism is also referred on item 2.1.2 and illustrated in Figure 6 (b).

Bubbles floating on the water phase also may increase their size if they collide and coalesce with bubbles rising with different velocities and/or because of the decrease in hydrostatic pressure. However, this effect of pressure drop due to liquid level in flotation systems are not so high, hence, this latter effect on the bubble size is small (Edzwald, et al., 2011).

Figure 2 illustrates a conventional dissolved gas flotation system.

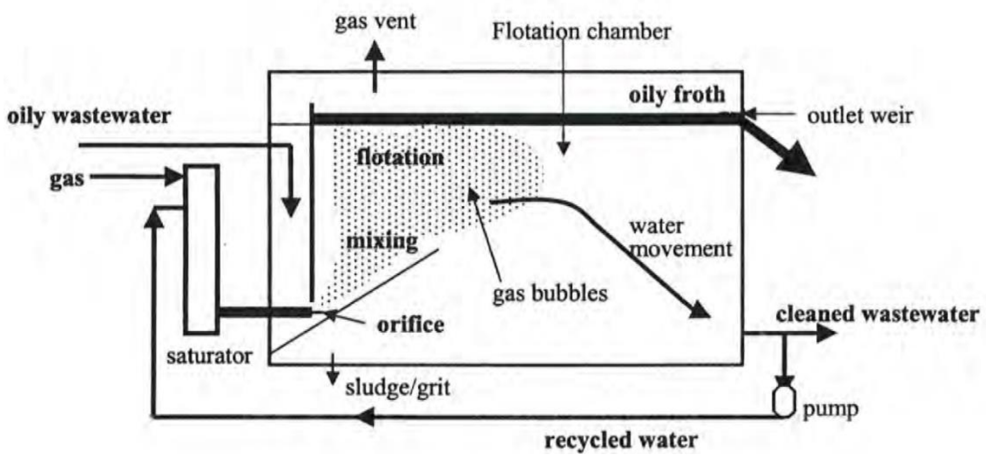


Figure 2: Scheme of a dissolved gas flotation system. Source: (Moosal, et al., 2002)

2.1.1.2. Induced gas flotation

The induced or dispersed gas flotation (IGF) also referred as IAF when air is applied as gas, was the initial type of flotation process implanted. In this process, gas bubbles are injected directly into the liquid phase. It started with earlier models using mechanical mixing impellers, where the rotatory motion spreads the bubble coming from a gas stream. Innumerous other devices where later deployed to supply the air in the system, like the jet-aeration – where a jet is created by the flow passage in elevated pressure through an orifice, the shearing action generates fine bubbles and promotes the inducement of gas in the flow, the splashing of the jet in the liquid surface results in gas entrainment, the aerated fluid are then oriented through a downcomer to the desired region (Clayton, et al., 1991); the pneumatic - where bubbles are formed by compressed air dispersion in perforated elements as porous layers (Eskin, et al., 2015); the hydraulic - where the injection device uses an eductor/ejector (venture tube principle) as a gas aspiration nozzle. When the motive flow (water) passes through the constricted section in the tube, it increases the velocity and lower the pressure, as a result, the gas is sucked up to the line. The gas can also be dispersed by means of nozzles, injected directly from a gas stream or by means of an aerated flow passing through an upstream pipe with a static mixer (Wang, et al., 2010) (Rubio, et al., 2002)

Compared to the DGF, the IGF has lower retention-time, it is less quiescent and uses a relatively large volume of gas. Its commonly multistage design permits better efficiency as well (Wang, et al., 2010).

Figure 3 illustrates a mechanical induced gas flotation system.

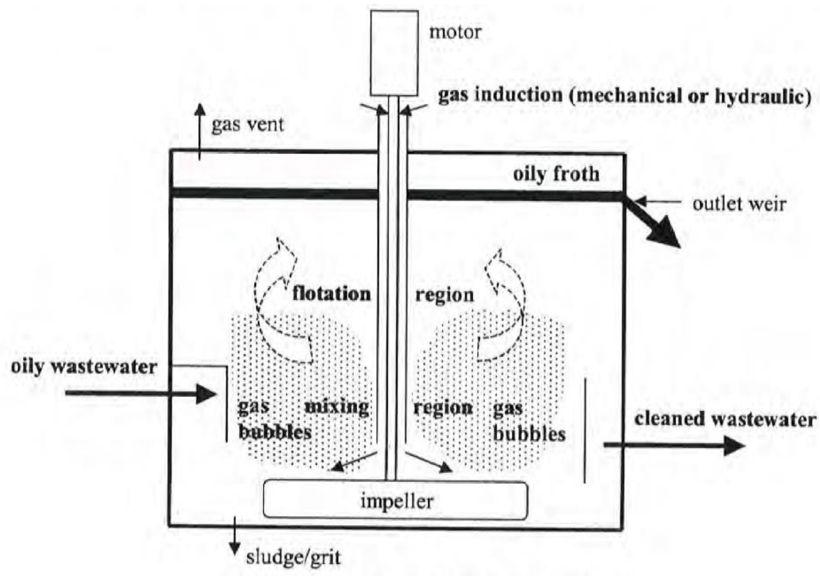


Figure 3: Induced Gas Flotation – Mechanical type. Source: (Moosal, et al., 2002)

2.1.1.3. Electroflotation

In electrolytic flotation or electroflotation, a direct current is applied between two electrodes, generally as a low voltage - in the range 5–20 V (Kyzas, et al., 2016). An electric field is built up between the cathode and the anode by the conductivity of the liquid. As a result, oxygen bubbles are formed at the anode and hydrogen bubbles at the cathode, as per the following reactions (Mansour, et al., 2007):

$$\text{Anode: } H_2O \rightarrow \tfrac{1}{2}\, O_2(g) + 2H^+ + 2\, e^- \ldots$$

$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \ldots$$

The relative quantity of gas produced is a function of current density and salinity of the solution (Kyzas, et al., 2016). The treatment unit is usually a rectangular tank with pair(s) of electrode grids near the bottom. Electrode materials include steel, aluminum, lead oxide deposited on titanium, and stainless steel (Edzwald, et al., 2011). Prime variables that affect current density, bubble size and numbers, etc. are pH, type of electrolyte (NaCl, HCl, NaOH), current density and retention time (Wang, et al., 2010).

The main advantage of the electrolytic flotation is that a large amount of very small bubbles is formed and with minimum turbulence. It has been reported bubbles size small as 20µm up to an average of 100µm (Mansour, et al., 2007)(Liuyi, et al., 2014). Another advantage is that the electrode grids can be arranged to provide good coverage of the surface area of the flotation tank. In this way, uniform mixing between the wastewater and the gas bubbles is achieved (Kyzas, et al., 2016).

Gas production, residence time and others operating conditions of electroflotation are easily controlled. Although these devices are reliable and safe for operation matters due to low voltage usage, it requires security measures to eliminate the hazard from the predominant escaping gas (hydrogen). A blower system can be applied in this case (Kyzas, et al., 2016).

Some disadvantages of the electroflotation are the power consumption and operating costs that are usually high, and the hydraulic loadings are low compared to the others flotation types, hence larger tank footprints are required. There is also the risk of contamination of the floated water with metals originating from electrodes. Other difficulties are electrode fouling, maintenance, and replacement.

Besides the flotation itself, other phenomena can contribute in the wastewater treatment with electroflotation. Without the addition of chemicals, a preliminary coagulation occurs within the suspension that seeks to group the positive and negative particles together. In addition, in the diffusion layer of the anode, free atomic oxygen is produced and then carried by convection into the suspension where it immediately combines and oxidizes organic and inorganic materials in the suspension. In a similar manner, there is also a production of hydrogen bubbles with concomitant reduction of some contaminants in the solution (Wang, et al., 2010).

Electroflotation can be used in cases where the available gas could be difficult to dissolve in a particular effluent. Some applications of this process are the treatment of animal waste, textile wastewaters, and industrial effluent containing emulsions and heavy metals (Edzwald, et al., 2011).

Figure 4 illustrates electroflotation systems to remove particles from wastewater.

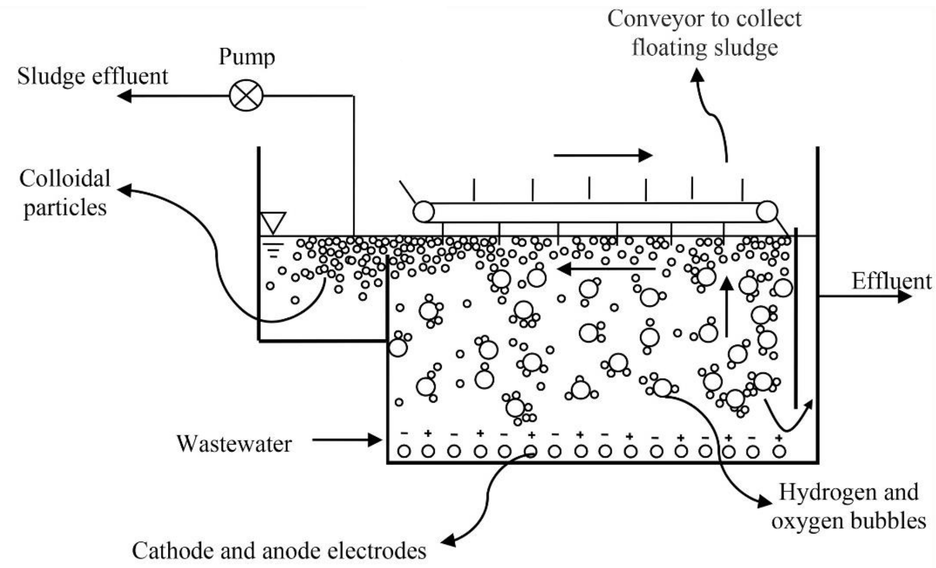


Figure 4: Example of an electroflotation systems. Adapted from: (Talaiekhozani, et al., 2017)

2.1.1.4. Gases used for flotation

Different gases have been used in flotation processes, with air being the most common. However, in some specific applications, like the oil production installations, air is not preferred due to the presence of oxygen that can bring up disadvantages such as: biological growth, adverse chemical reactions and corrosion that end up in precipitations, for instance, of iron oxides and sulphides, that can lead to scale issues (Rawlins, 2009) Moreover, there is a safety risk due to the explosive possibilities when oil is combined with oxygen.

For produced water treatment, frequently natural gas sources available in the facility is used due to the convenience and compatibility with the influent. Using field gas, the risk of corrosion/scale is minimized. In addition, if the water is to be reinjected into the reservoir, the use of natural gas makes unnecessary further oxygen removal from the water to prevent rusting of tubulars. Apart from these gases, nitrogen and carbon dioxide are also being used in some specific gas flotation processes (Moosal, et al., 2002)(Saththasivam, et al., 2016). For the electroflotation, as already mentioned, the gas (oxygen and hydrogen) in generated on the electrodes by means of electric field.

2.1.2. Contact/collision between gas bubbles and particle

For a bubble to get in contact with a particle, the system hydrodynamics shall favors collisions. The collision probability between bubble and particle is then highly associated with the gas/particle ratio as well as their individual concentration and size. Collision may occur by the upward motion of the bubble that can reach a (downward/slower-upward) particle - if they are in the zone of collision with favorable hydrodynamics, and/or facilitated by a turbulent environment. This phenomenon is illustrated on Figure 5. This latter collision mechanism is called by some authors as fluid shear collision. Velocity gradients may result from mixing devices or continuous flow in the equipment (Edzwald, et al., 2011).

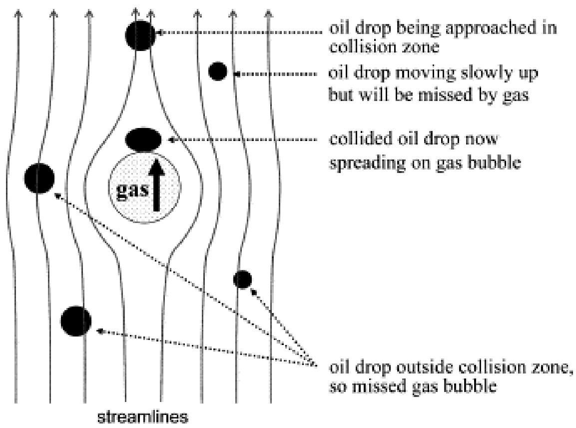


Figure 5: Example of (miss)collision between oil droplets and bubble. Source: (Moosai, et al., 2003)

For particles less than about 1µm, however, fluid shear is less significant. In this case, Brownian diffusion prevails. It produces collisions among small particles because of random displacement of water molecules (kinetic energy) striking particle surface (Edzwald, et al., 2011). As the efficiency is smaller for these minor particles, it is recommended to grow the droplets by coalescence to about 20µm, which may be achieved by chemicals additives as surfactants and demulsifiers – that will be discussed further (Moosal, et al., 2002).

The collision can also take place by bubble clusters. This group of bubbles held together by bridging particles that are simultaneously attached to two or more particles facilitates particles entrapment. In the DGF, it can also happen that the bubble nucleates on the particle surface – as seen on item 2.1.1.1, i.e., the bubble is "born" in contact with the particle. In addition, small droplets can also be captured by the hydrodynamic profile in the aft-end of uprising of big bubbles. Particles shall be sufficiently small to keep trapped in the bottom of the bubble, as chemical adhesion may not occur. This last mechanism does not create a strong bond, though (Rawlins, 2011). Figure 6 bellow presents examples of collisions.

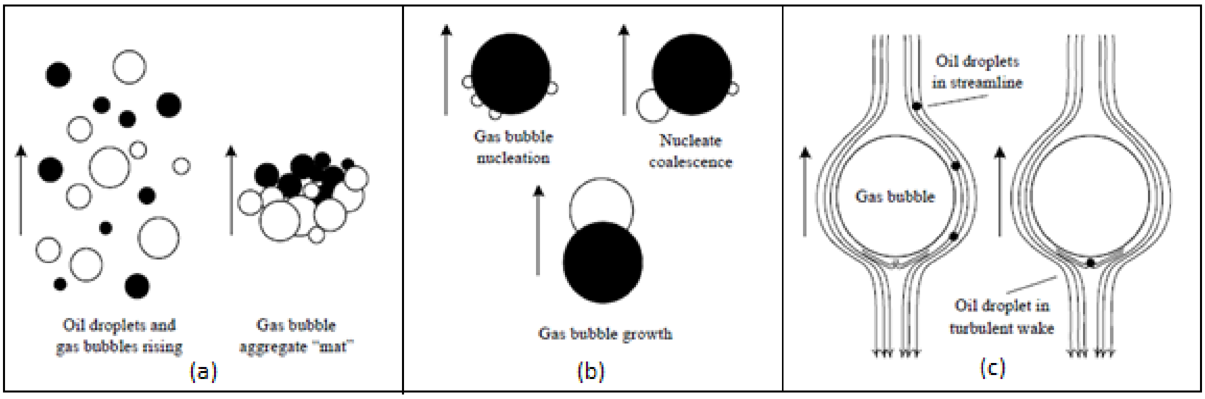


Figure 6: (a) Gas bubble clustering; (b) gas bubble nucleation, coalescing and growth; (c) hydrodynamic capture of oil droplets in the wake of a rising gas bubble. Adapted: (Rawlins, 2011)

2.1.3. Attachment of gas bubbles

The adherence upon contact between the particle/aggregate and the gas bubble depends on the resulting forces at the gas–water–particle interface deriving from physical attraction forces and physicochemical repulsion forces (Wang, et al., 2010).

In DGF, small bubbles can attach into particles by nucleation, as seen before. When collision occur between the small bubbles and small particles, various particle-bubble forces are considered. The most important forces in this case are electrostatic repulsion or attraction, van der Waals forces, hydrodynamic effects and hydrophobic effects (Edzwald, et al., 2011).

Bubble attachment to large particles (>100µm), as the case of IGF, is characterized by the contact angle measurement of this forces, as illustrated in Figure 7 (a). Solid surfaces are often naturally wettable by water and termed hydrophilic. A surface that is nonwettable, as the oil droplet, is water repelling and termed hydrophobic. If a surface is hydrophobic, it is typically air attracting termed aerophilic, and it is strongly attracted to an air interface, which readily displaces water at the particle´s surface, as shown in Figure 7 (b) (Wang, et al., 2010). The magnitude of the contact angle is related to particle hydrophobicity and adhesion to the bubble. Hydrophobic particles have large contact angles (>90degrees) and good separation by flotation (Edzwald, et al., 2011).

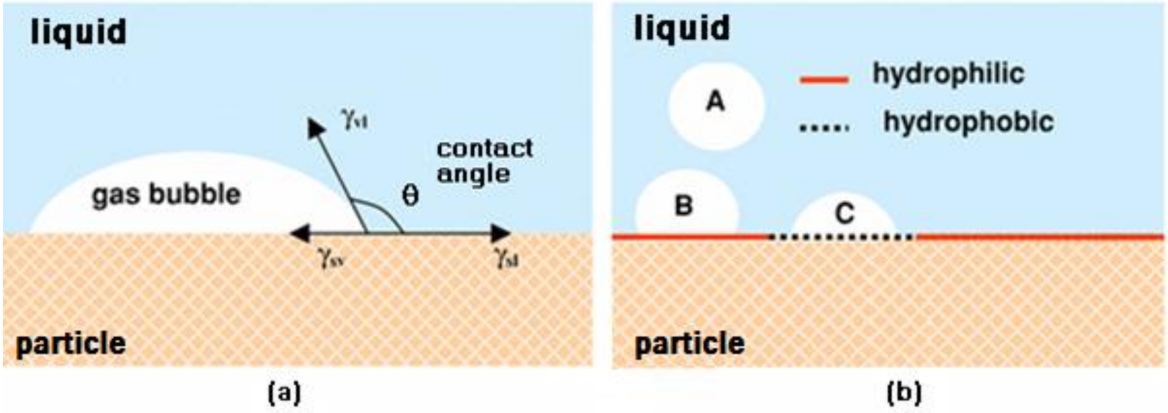


Figure 7: (a) Contact angle of three-phase interfaces. Υ_{vl}, Υ_{sv} and Υ_{sl} are the surface tension of liquid–vapor, solid–vapor and solid–liquid, respectively, and θ is the contact angle of liquid on the solid surface. (b) Schematic drawing illustrating a floating bubble (bubble A), hydrophilic surface (bubble B) and a hydrophobic surface (bubble C) – Note larger angle. Adapted: (Meng, et al., 2006)

Some particularities of oil droplets make the attachment process more challenging compared to solid irregular particles, as mineral grains. Oil droplets in small sizes are nearly perfect spheres which means that the surface area for attachment approach is in its minimum for a given volume. Oil droplets also have a deformable surface (as well as bubbles) and undergo an elastic collision/attachment process with gas bubbles. Thus, the collision can result in a rebound, rather than attachment. Moreover, applications in the oil and gas industry mostly handle hypersaline (up to 300,000 ppm dissolved solids) solutions (produced water) and utilize natural gas, both of which affect the interfacial tension between the three-phase droplet-water-bubble system. Charges of such gas are similar to the oil and create repulsive forces. To overcome that, chemicals, like surfactants, are needed to neutralize the electrostatic forces (Rawlins, 2011).

The attachment steps are shown on Figure 8 (a-e). When an oil particle reaches out a bubble, it slides around the bubble surface until the separation distance is within the range of surface forces, and a thin layer of water is created. The surfactant concentration varies along the created thin film, causing a gradient in the interfacial tension along the surface. The liquid is squeezed out of the thin film when particles get closer. As the liquid drains, due to the interfacial tension gradient, a characteristic dimple is created. The dimple disappears as liquid film drains further until its rupture when it reaches a critical thickness. The minimum time for film thinning, rupture and formation of a stable bubble-particle aggregate is defined as the induction time (Xinga, et al., 2017)(Moosai, et al., 2003).

For small oil particles, as in oil in water emulsions, contact of oil droplet and bubble gas may result in the full encapsulation, where the oil spread in the bubble surface providing a strong bond, thus preventing removal by shear forces. Such mechanism also fosters the attraction of free oil droplets, improving flotation effectiveness. If the droplet size is insufficient for full encapsulation, a lens shape may form behind the bubble, to minimize contact with the aqueous phase. A third attachment type may occur with the oil droplet that is the creation of a contact point with the gas bubble (Rawlins, 2011). These mechanisms are illustrated on the Figure 8 (f-h).

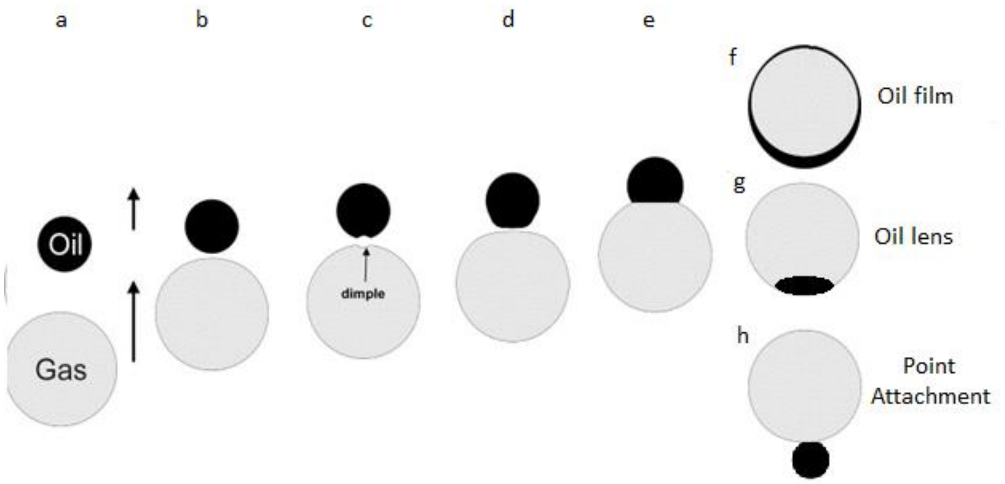


Figure 8: Mechanism of small droplets collision and adhesion:(a) Bubble and drop approach; (b) water film thinning; (c) thin film dimples due to interfacial tension gradients; (d) the dimple disappears as film drains and thins further; (e) at a critical thickness film ruptures, and if spreading conditions are present, the oil spreads around the gas (f), or it forms a lens (g) or a point attachment (h). Adapted: (Moosai, et al., 2003)(Rawlins, 2011)

Surface chemistry of particles, solution chemistry and surfactants and surface forces are important parameters in this stage (Xinga, et al., 2017). Due to the relevance of the chemistry and effluent conditioning in flotation processes, there is a dedicated topic concerning pretreatments and chemicals in item 2.5.

2.1.4. Rise of the aggregates to the concentrate phase

Fallowing the steps in the flotation process, once droplets attach to a bubble to form a floc/aggregate, the resulting force of gravity and buoyancy will lead to an upward motion. The flocs flow through the medium in the device and are collected in the surface (in a usual design). The effluent velocity shall be inferior to the bubble rising velocity in order to enable floc separation. The flow rate will define the residence time. Although large residence times increase the probability of bubble-particle collisions, elevate retention time may cause deterioration and splitting-up of flocs (Scholz, 2006). The detachment of particles may occur from perturbations in the surrounding environment or by bubble coalescence and/or bursting during the transport of these aggregates to the froth phase.

A combination of different mechanisms is involved on knocking the particles off the bubbles in turbulent flow. The most known is caused by the swirling motion of fluids (eddies) that takes place in turbulent flows. According to a traditional theory about particle-bubble detachment (Schulze, 1982, 1997), an eddy may dislodge the particle from the surface of the bubble. According to this, the aggregate may be trapped inside an eddy and the particle rotates on the surface of the bubble along with the eddy. The particle on the surface experiences a centrifugal force as a result. If the centrifugal force exceeds the surface tension forces that tend to keep the particle attached to the bubble, the particle detaches. This rotation of a particle on the surface of a bubble, nevertheless, is possible only when the particle-bubble aggregate interacts with an eddy of comparable size to the bubble. When the aggregate interacts with an eddy much larger than the bubble, the particle can detach due to differences in direction between it and the bubble (Wang, et al., 2017). A scheme showing its phenomena is displayed on Figure 9.

To reflect the extent of the interactions between the particles and the eddies a dimensionless number can be used, the Stokes number (eq. 3) - shown below and illustrated on Figure 9.

$$St = \frac{a^2 U}{3\beta \nu L} \quad \text{(Stokes number)} \qquad (3)$$

Where **a** is the radius of the particle, **v** is the water viscosity, **L**is the length scale of the eddy, **U** is a representative flow velocity and the density ratio, **β** is the density ratio, presented in eq. 4:

$$\beta = \frac{3\rho_f}{2\rho_p + \rho_f} \quad \text{(Density ratio)} \tag{4}$$

Where ρ_f is the density of the fluid and ρ_p is the density of the particle.

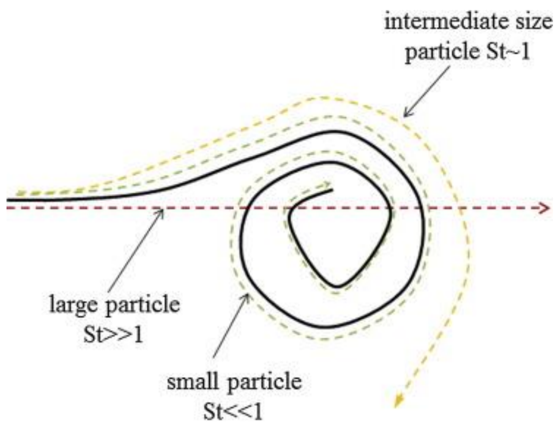


Figure 9: Schematic view of an eddy with the particle dispersion by different Stokes number. A particle with a large Stokes value is almost insensitive to the presence of the eddy (the green, yellow and red lines correspond to increasing Stokes values, respectively).
Source: (Wang, et al., 2017)

Wang, *et al.* (2017) in a recent study, point out two other modes of particles detachment from bubbles: (i) Rapid changes in trajectory of the bubble: when the bubble accelerate or decelerate faster than the neighboring flow of liquid in turbulent fields - because of its inertia, the particle kept moving, ultimately leaving the bubble; and (ii) due to oscillations in the bubble surface either from bubble coalescence process or from interactions with pressure fluctuations in turbulent fields. The inertial force dislodges the attached particles only when the bubble surface oscillates at a high frequency and magnitude.

It is believed that among all the factors related to particle-bubble detachment, the one that contributes most are eddies of same length scale as that of the particle-bubble aggregate (Wang, et al., 2017).

Bubble coalescence in the froth phase, bubble bursting on the surface and a stagnant froth region should also be minimized in order to maximize froth recovery from the attached particles in the concentrate phase. Nonetheless, for wastewater treatment stable foams is less important than for mineral flotation (Rubio, et al., 2002).

2.2. Flotation system performance

Estimation of the flotation recovery efficiency (**E_{Flot}**) is very complex due to the wide number of parameters affecting the process. The general model applied for this process (Dai, et al., 2000) states that the probability of a particle reaching the surface depends on the success of 4 key phenomena that occur under the process steps described below on eq. 5:

$$E_{Flot} = E_c \,.E_a \,.E_s \,.E_f \quad (5)$$

Where, **E_c** is the collision efficiency i.e., the ratio of the number of the particles encountering a bubble. This term is highly dependent on the concentration and size of both particle and bubble; **E_a** is the attachment efficiency, which is proportional to successful collisions. As it is greatly related to surface properties, the use of chemicals enhances this efficiency; **E_s** is the particle-bubble aggregate stability efficiency, and accounts for the detachments; **E_f** is the efficiency of transport of particles through the froth phase, it considers the recovery of the attached particles out of the froth zone transportation. Not all researchers take into consideration this last term.

Each of these terms are objects of study from many researches. Several models to estimate collision was reviewed and tested by Dai, *et al.*,(2000). Attachment efficiency models are less developed than collision models, and the existing ones do not have universality of applications (Xinga, et al., 2017). Some of them were analyzed by Ralstopn, *et al.*, (1999). Different detachment models have been reviewed by Wang, *et al.*, (2006) and grouped into three principal categories: force balance, energy balance and maximum floatable particle size. Comparatively to other terms, less papers were found related to the transport modeling. Two of them are Zheng, *et al.*, (2004) that gives a brief review of froth transportation together with transport model, and Neethling, *et al.*, (1999) that developed a model with close correspondence to experiments.

2.3. Historical and economical aspects of flotation

The origin of the flotation process started from the mineral processing, it has been used for many years in the beneficiation of ores. Up to the middle ages, minerals were separated by hand and later improved to gravity separation. In 1860 in England, it was found out the affinity of small particles to adhere to oil droplets, which could concentrate the particles in a surface layer from a watery suspension, as the oil rose to the top. The principle of bulk oil flotation was thus born. In 1877 in Germany, it was discovered that faster separation was achieved if air was added to the suspension. This process was patented. By 1912 no less than 140 different patents that had some connection with flotation have been registered with oil alone or aided by air (Edzwald, et al., 2011). Its first application in wastewater treatment field was flotation of suspended solids, fibers, and other low-density solids. The industrial application in this field really began around 1970 with earlier models using mechanical mixing impellers (Wang, et al., 2010).

In first decade of 20th century, different methods of introducing air into the flotation system were proposed. The mining industry was quick to capitalize on these inventions. After experimentation with the numerous technical possibilities of introducing air into the flotation tank, the applications for mineral separation soon converged on the direct injection of air, or dispersed air flotation, which remains the method of choice in the mining industry to this day. The further development of flotation for mineral separation therefore focused on finding more efficient collectors and frothers (Edzwald, et al., 2011).

Chemistry innovations also contributed significantly to improvements in flotation processes. Mainly considering that throughout history properties of effluent got more challenging (quality of ore declined, oil in water emulsions treatment required), environmental impacts attracted more concerns (increasing governmental restriction) and economic pressures got tighter (commodities price fluctuation and marketing competition) (Nagaraj, et al., 2016).

<u>Overview of installed flotation columns around the world</u>

The Harbort, *et al.* (2007) made an analysis showing the installed flotation columns around the world, classified in its study as non-mechanically agitated flotation machines. They utilized Amec Foster Wheeler flotation database containing 4000 installed flotation columns. From this data it was possible to build up an historical distribution of installed column since 1961, as presented on Figure 10, the geographical distribution from the cumulative number per country, as presented on Figure 11, and the cumulative proportion per region, illustrated on Figure 12.

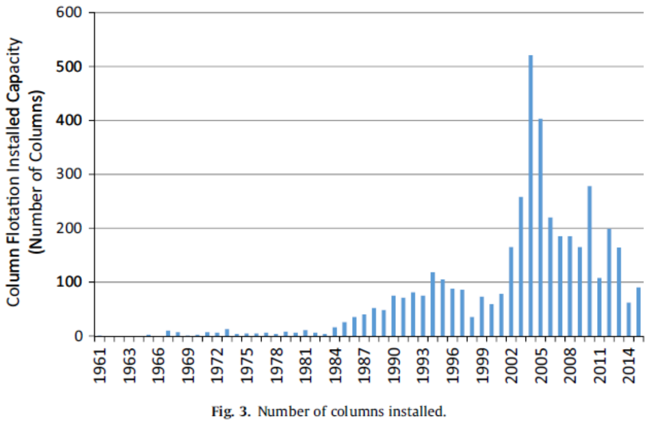


Figure 10: Number of columns installed per year based on the Amec Foster Wheeler database. Source: (Harbort, et al., 2017)

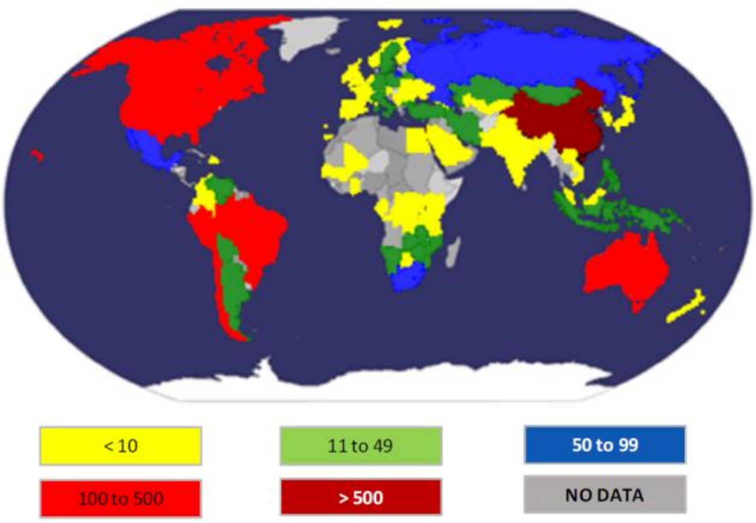


Figure 11: Cumulative number of flotation column installed per country. Source:(Harbort, et al., 2017)

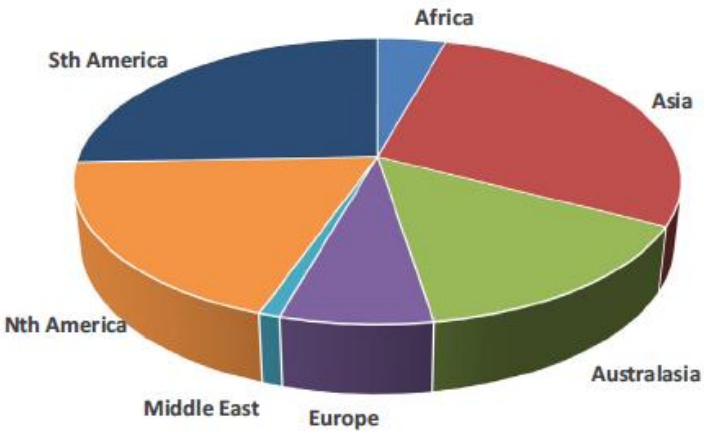


Figure 12: Flotation columns installed per geographical region - the cumulative distribution of installed flotation column area per geographical region since 1961. Source: (Harbort, et al., 2017)

As shown on Figure 17, since 1961 column flotation has gone through three distinct rises and falls in popularity. The reasons for historical fluctuations are wide and varied. According to the author, fluctuations in commodity prices have possibly being the most pronounced factor affecting the popularity, other reasons are related to the rise and fall of individual flotation column manufacturers, the necessity for circuit refurbishment, commodity specific requirements and the effect of capacity saturation, both within commodities and individual countries (Harbort, et al., 2017).

An analysis of Figure 11 and Figure 12 shows the column flotation highly spread around the world, with northern Africa the only region without registered installations. China clearly dominates flotation column installation with over 1000 units installed. Australia, Canada, USA, Chile, Peru and Brazil also recorded substantial installations. Column flotation also plays a significant role in Mexico, South Africa and Russia. However, it is important to take into consideration that not all installations are recorded in the database, so this figure may underestimate the number of flotation columns installed (Harbort, et al., 2017).

2.4. Flotation devices

The main flotation units are circular and rectangular, with the former being the most popular due to its economical construction; better bubble distribution (almost uniform distribution over the horizontal section); low velocities maintained throughout the active flotation zone; lower cost for implantation and maintenance such as pivoted arm skimmer, bottom scrapers, drive shaft; it can be also the case of a converted sedimentation tank. On the other hand, the rectangular geometry is advantageous for space conservation in congested areas; most standard sizes can be shipped set up, thus minimizing field erection; it is easier to control the side entry of streams compared to the center inlet of a radial flow in an circular tank unit; in addition, the use of a hopper bottom eliminates the need for bottom scraper (Wang, et al., 2010)(Edzwald, et al., 2011). For the treatment of water and wastewater, generally rectangular units are chosen as they can be constructed as a monobloc together with the flocculator and filters (when it is the case), so that land requirements are minimal (Scholz, 2006). In an offshore application, due to the strict footprint requirement and motion of the platform, vertical (circular columns) unit and no moving part is preferred – It both minimizes unit area, and allows a thicker oil skim pad which is much less sensitive to platform motion (Rawlins, 2009).

It is common to name two regions inside the flotation cell: the contact zone (also called reaction zone and mixing zone) situated in the front portion of the unit where the flocs get in contact with the bubble, and the separation zone, the region where the aggregates rise to surface. The contact zone requires a minimum agitation to promote particle bubble collision, and in the separation zone the turbulence is reduced - a quieter flow is set to avoid detachments (Edzwald, et al., 2011). These regions are illustrated on Figure 13.

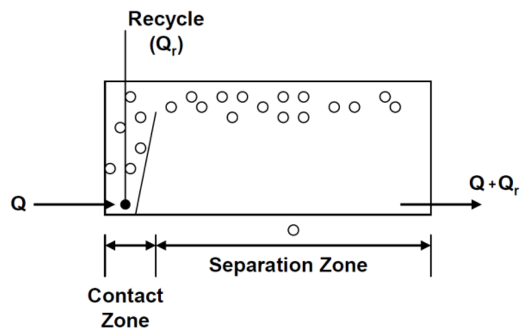


Figure 13: Schematic illustration of contact and separation zone. Source: (Edzwald, et al., 2011)

Two main variables govern the design: the downward velocity and the quantity of particles to be floated per unit area and time. As set before, the water downward velocity shall be slower than the rise velocity of the bubble in order enable the separation and avoid the bubble carry over. The more uniform is the distribution of water and microbubbles, the better. In general, the water to be treated is introduced in the top half of the unit. The clear liquor outlet is fitted in the lower third of the unit. Sludge/concentrated phase is collected usually at the open surface. On circular unit, scrappers can push the sludge into a radial collection channel. In rectangular model, it is common that the sludge is pushed by a series of scrapers driven by endless chains to a removal channel situated at one end. Besides the scraper mechanism, the concentrated phase can be removed by over boarding in peripheral chambers or collected by immersed headers (Scholz, 2006, 2016).

A variety of design aspects can be incorporated in the equipment in order to adapt for different scenarios and/or improve performance. They are: <u>swirling flow</u>, that may use centrifugal force and promote gradient velocities; <u>column flotation</u>, that consist of a unit with superior proportions of high: length, minimizing footprint. Flow pattern can be counter current with the bubble in which the inlet enter in the top region and the gas is fed in the bottom part, or co-current with both inlets near the bottom - in this case special internals are require to route the clean phase to and appropriate exit; <u>coalescing media</u>, applied in oil removal systems to help coalescing droplets by capturing and enlarge particles - types include corrugated plate, balls and saddles (Rawlins, 2009); <u>loop flotation</u>, that consists of two concentric tubes in which the gas are fed in the bottom of the central region (riser) causing an air-lift. The inner tube fluid then flows with upward velocity and the fluid in the annular region (downcomer) flows downwards generating an internal circulation (Qi, et al., 2013).

There are several device models reported in the literature with specific characteristics such as the <u>compact flotation unit</u> (CFU) that is reported on literature as a generic vertical hydraulic single cell with many option of designs. In industrial area, however, it commonly refers to a device that makes use of a rotational flow and has special fixed internals for mixing gas and particles, the gas generation method can be induced or dissolved and it has for some cases options for multiple stages within one vessel (Rawlins, 2009)(Bhatnagar, et al., 2014); the cyclonic-static micro-bubble flotation column (FCSMC) that combines the column flotation on an upper part, a cyclonic separation on the bottom and a micro-bubble generation by jet pipe device (Li, et al., 2016); the Jameson cell, that by means of a distributor splits the flow through several downcomers in elevated pressure, the gas is induced by jet and is fed in the mixing zone (Clayton, et al., 1991), some variations has been developed since its creation (Cowburn, et al., 2005). Examples of these models are shown on Figure 14, Figure 15 and Figure 16.

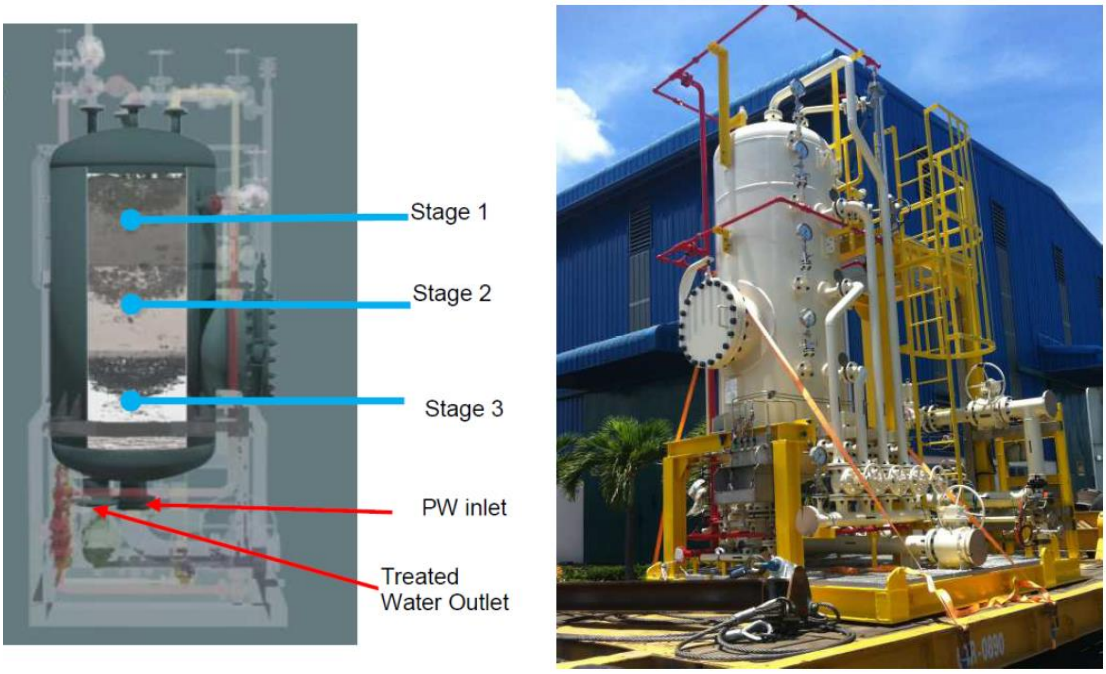


Figure 14: A scheme and picture of a compact flotation unit. Source:(Bhatnagar, et al., 2014)

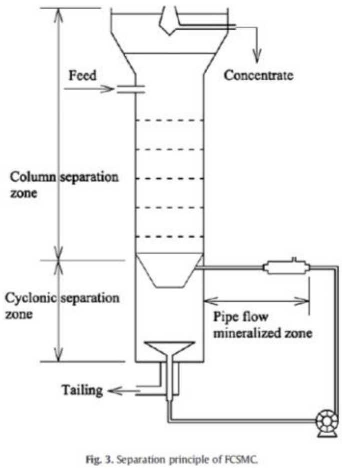


Figure 15: Scheme of a FCSMC. Source: (Li, et al., 2012)

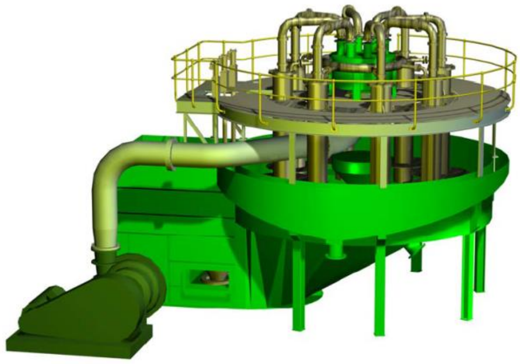


Figure 16: Schematic of a Jameson cell (Z Cell type) Source: (Cowburn, et al., 2005)

2.5. Chemicals and pretreatments

Most of the flotation systems employ chemicals in its process. Those chemicals have several functions as emulsion breaking, floc formation, selection of (un)desired materials, improve performance, etc. The chemicals can be added in the upstream pipe, directly in the flotation cell or in pretreatment stages with dedicated units. In order to disperse the chemicals, some rapid mixing alternatives are: providing turbulent energy from an impeller or turbine mixers, pipe injection, in-line static mixers, open channel static mixers and upstream pumps - make use of head loss through pipe elements (Edzwald, et al., 2011).

In the treatment of water for different areas, it is often required the conditioning of the influent to enable the flotation process. The two most common pretreatments are coagulation and flocculation. Both modify the charges between particles and particle-bubble interfaces. This can be achieved by surface active agents – the surfactants. Surfactants are characterized for having two essential portions: one hydrophobic comprising hydrocarbon groups with a linear chain, and one hydrophilic comprising groups such as sulphate, sulphonate or ethoxylate – if this portion has a high molecular weight, it is termed a surfactant polymer. Surfactant are divided in four categories according to the distribution of electrical charge: anionic, cationic, non-ionic, and amphoteric. Nowadays in oily wastewater industrial practice, cationic and anionic surfactants and polymers are used. Besides neutralization of charges, the polymer long chain enables mechanical bridging of particles to create flocs. The longer the polymer, the bigger the molecular weight. It is common to find dedicated stages for these two pretreatments as both demand mixture, as shown schematically on Figure 17 (Moosai, et al., 2003)(Edzwald, et al., 2011).

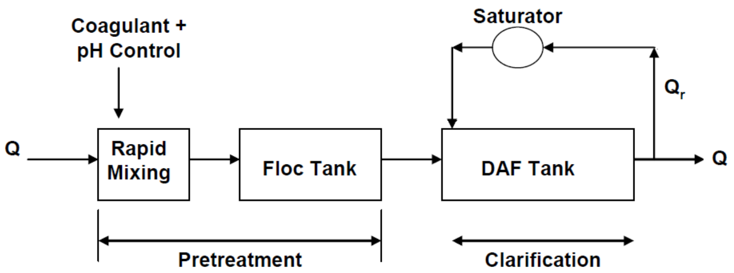


Figure 17: Schematic of Pretreatment in a flotation system. Adapted: (Edzwald, et al., 2011)

Coagulation

The main purposes of coagulation are: to destabilize particles as in the de-emulsification of oil in water emulsions, to convert soluble material into insoluble as in the precipitation of dissolved organic substances, and to produce particles with a relatively hydrophobic character. Tiny droplets from oil in water emulsion (lower than 20 micron) are prevented from coalescing by negative charges on the surface of the droplets and gas bubbles due to electrostatic forces created by the electric double layers. These create a repulsive force between the drops or bubbles which keep them apart (Moosal, et al., 2002). Coagulation is achieved by neutralizing the particles to little or no net electrical surface charge and thus, greatly reducing the repelling force between the particles. Surfactants applied in this stage has low molecular weight and are called coagulants (demulsifiers). Chemicals often used in this application are aluminum or ferric salts, as can be observed on the Table 2.

Table 2: Coagulants used in flotation systems. Adapted from (Saththasivam, et al., 2016)

Coagulant	**Optimal dosage (mg/L)**	**Optimal pH**	**Influent concentration (mg/L oil)**	**Removal efficiency**
Alum	600-800	6,93 ±0,2	169,7±17	78,59 ±0,8%
Alum	800-1400	8 - 10	-	99% COD removal
Aluminium Sulphate	50	4	500	93%
Aluminium Sulphate	100	8	1630	99,3%
Ferric Sulphate	120	7	1630	99,94%
Ferrous Sulphate	700-1000	8,9 ±0,2	169,7±17	72 ±4,2%
Ferric Chloride	100	6	500	>95%
Ferric Chloride	500-700	8,41±0,15	169,7±17	73±5%

<u>Flocculation</u>

The flocculation function is to agglomerate the particles into (macro)flocs. By enlarging the size of the particle, the collision probability with the bubble is increased and a faster rise velocity is obtained. Chemicals applied for this purpose are called flocculants, they are surfactants with high molecular weight. Information about commercially used chemicals composition is not often divulged (Moosai, et al., 2003).

Figure 18 below shows sequence stages of the flotation treatment of oily emulsion pretreated with a flocculation polymer.

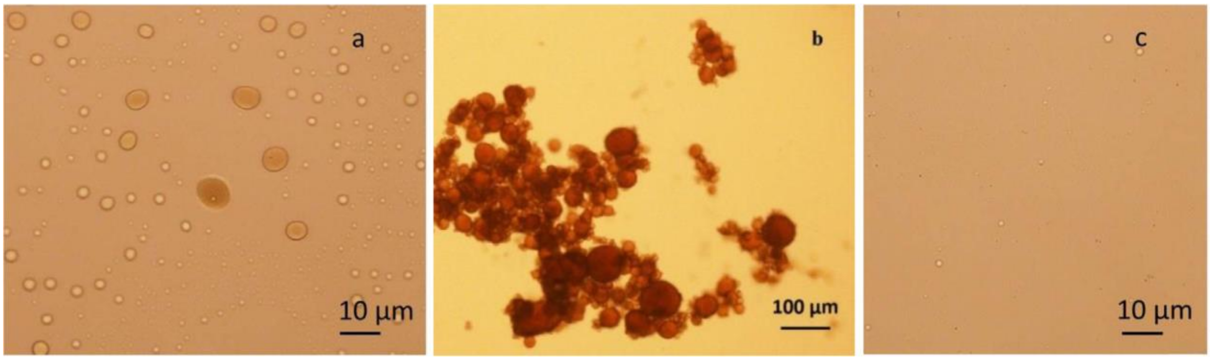


Figure 18: Microphotographs of different stages of oily emulsion: (a) after free oil phase separation; (b) oily flocs after flocculation ; and (c) treated water by flotation. Source: (Etchepare, et al., 2017)

The chemistry of coagulation and flocculation involves selecting proper dosing and pH adjustment once it affects the charge of the flocs and the solubility of metal coagulants (Edzwald, et al., 2011). Experiments must be carried out to identify suitable chemicals, their concentration and process conditions. This can be done using bottle test, jar-test or a small-scale apparatus (Moosal, et al., 2002)(Moosai, et al., 2003).

Each application of flotation process requires its own chemical according to the purpose and characteristic of the fluid being treated. In this work it was focused on the oily water treatment demands. Chemicals related to mineral processing were also summarized and can be found on item 2.7.

The importance of the chemicals and its synergy with the flotations process is highlighted by Nagaraj, *et al.* (2016): "*The evolution of flotation chemical technology over the past 100 years is reflected in the growth in diversity and tonnage of chemicals used. Innovation in the development and use of chemicals has gone hand-in-hand with innovation* *in the development of flotation technology. The introduction of chemicals made the flotation process practical and widely applicable; conversely, developments in flotation technology made possible the use of a wider variety of chemicals. The resulting positive feedback of this relationship led to the development of improved flotation operations.*"

2.6. Oil sands

A way of exploring and producing oil is by oil sands resources. Oil sands is naturally occurring sands saturated with extremely heavy form of petroleum called Bitumen or bituminous sand. The common method of separating the oil from the sand is the hot water extraction processing. It utilizes hot water (5OºC - 80ºC) and caustic soda (NaOH) to condition the oil sands. This process decreases oil viscosity due to the temperature increase, and releases natural surfactants from the bitumen due to the addition of caustic and increase in pH. The fluid is then transferred to a gravity separation tank - the primary separation cell (PSC), where most of the oil is withdraw from the surface layer. The waste product, drawn from middle/ bottom of the PSC, is sent to a tailing area and further treated by flotation process to recover the remaining bitumen (Nassif, et al., 2014)(Loganathan, et al., 2015). The estimated water consumption in this process is approximately 3 barrels of freshwater for every barrel of oil produced (Alam, et al., 2017).

2.7. Mineral

Rubio, *et al.* (2002) overview report considers a "bridge" within flotation process applied to various engineering fields including the mineral processing and the wastewater treatment. He expresses his beliefs on the cross exchange of flotation experience from both applications to lead to new and improved procedures for the industry waste treatment. Some of the differences between these two areas are: mineral processing operates with medium and large bubble sizes, while the wastewater usually requires microbubbles; less shear rates is applied in the waste treatment due to presence of aggregated colloids; the particles involved as in the mineral flotation the ores are solids while in the waste there is the presence of liquid droplets; mineral flotation requires a more stable froth; additionally, he points out that "*in mineral flotation, the overall process is economically attractive. In environmental application, usually flotation means an extra cost*".

Rawlins (2009), in addition, loosely (his words) classifies crude oil as mineral by using the definition "*any naturally occurring homogeneous substance or compound that results from the processes of nature and obtained usually from the ground*". He highlights also the difference of flotation applied to an offshore facility where footprint requirements are too strict, and motion should be take into consideration. In addition, he adds that units working with natural gas such as in oil and gas industry, flotation chamber shall be fully encapsulated to prevent hydrocarbon vapor release into the atmosphere.

Table 3presents some parameters of flotation in mineral processing and in wastewater treatment for comparison.

Table 3: Differences between flotation in mineral processing and in wastewater treatment. Adapted from: (Rubio, et al., 2002) and (Matiolo, et al., 2003)

Parameter	**Mining Flotation**	**Water/Waste Flotation**
Feed solids content (weight/weight basis) (%)	25-40	<4(DAF) 10-30 (jet/columns)
Particle size to float (µm)	10-150	1-50 (non flocculated) and 1-5mm (flocculation with polymers – aerated flocs)
Bubble size distribution (µm)	600-2000	30-100 (DAF) 100-600 (jet/columns)
Bubbles rising velocity (m/h)	250-800 (approximated values)	0,7-30(DAF) 30-1000(Jet/columns)
Number of bubbles/cm^3	9x10^3 – 2x10^2	6x10^8 – 2x10^6(DAF) 2x10^6 – 9x10^3(Jet/columns)
Bubbles surface area (cm^2/cm^3)	100-30	4000–600 (DAF) 600–100 (jet/columns)
Air hold up (%)	15-25	8–14 (DAF) 20–40 (jet/columns
Particle material type	Cristaline solids, incompressibles	Mix of small crystalline solids with colloids, amorphous flocs and compressibles
Separation type	Solid/solid-liquid	Solid/liquid; Solid/liquid1/solid2; Liquid/liquid

Overview of mineral flotation process

Flotation is considered as the best process route for metal enrichment in the mining and mineral industry due to its wide range of application and ease of operation and implementation. After a rock is mined, it is typically crushed to a slurry consistency and then diluted with water to form a pulp. The liquid portion of the slurry is typically water. Based on the differences of surface properties between valuable minerals and gangue, it concentrates the valuables. Hydrophobic particles are selectively attached on gas bubbles rising through the pulp, they come together in the form of froth on the surface and then is separated. Flotation type are mostly the induced gas for having lower cost and because bubbles about 2mm are formed in this process – a required size to attain adequate buoyance for the mineral particles which are heavy (Edzwald, et al., 2011).

The physic-chemical property of the slurry is often adjusted with additives to assist in recovering a target component depending on the constituent species of the slurry. Therefore, the mineral flotation usually relies on the use of various chemical reagents (e.g., collector, frother and depressant) that affect the floatability of individual lore components.

For example, in the recovery of iron ore, various types of starches are used to depress the bubble adhesion response of iron ore so that only silica can be floated in the froth from the slurry. If the depressants are not added, a portion of the iron ore will also adhere to bubbles and float within the froth (Wang, et al., 2010).

Chemicals for mineral processing:

Collectors are hydrophobizing reagents, that render hydrophobicity to the mineral surfaces. They have a hydrophilic polar functional group and a non-polar hydrophobic tail with which they can attach to both particle and bubble at the same time, hence facilitate the contact of air bubbles and particles. Collectors include fuel oil, fatty acids, xanthates, various amines, etc.(Mankosa, et al., 2015).

Frothers are surface tension modifying reagents. They stabilize suspensions to avoid the collapse of bubbles and the settling of particles. There are many types of frothers, including alcohols, glycols, Methylisobutyl Carbinol (MIBC), and various blends.

Depressants are used to reduce the hydrophobicity of a specie – the opposite function of the collectors.

Because the pH of the slurry can affect froth formation, other chemical additives are introduced to modify the pH of the slurry. Acids or bases are added as needed to adjust the pH depending on the composition of the slurry.

Figure 19 shows an image of a mineral aggregate in a bubble-particle attachment test.

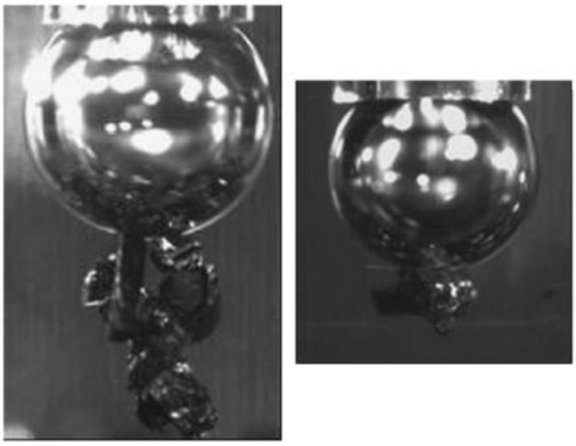


Figure 19: Picture of coal aggregate during a bubble-particle attachment experiment. Source: (Albijanic , et al., 2010)

In addition to the mineral processing, several other industries use gas flotation in the treatment of waste, for example: chemical processing and manufacturing plants, paper industry, ship bilge and ballast waste, deinking operations, meat processing, laundries, plastics recycling, metal plants, soap manufacturing, drainage cleaning, equipment washing, glass plants, soil remediation, soybean processing, mill waste, among others (Wang, et al., 2010).

2.8. Oily water

Oily wastewater is found in discharged wastes from residence and restaurants and greatly generated from diverse industries handling or producing oil. Major sources are petroleum refining and petrochemical plants, steel and metal manufacturing plants, metallurgical industries, and oil spillage in the sea. Oily wastewater causes serious problems if discharged in surface water like lake, rivers, and seas due to the low oil natural degradation rate. Hydrocarbon oils are also toxic, even at low concentrations, to biodegrading microorganisms present in conventional sewage treatment systems. Moreover, the oil layer in the water surface hinders the natural oxygenation process preventing the solar radiation penetration, thereby jeopardizing aquatic life (Kundu, et al., 2013). Health and environmental issues caused by these wastes made governmental regulating agencies to set strictly discharge limits. In Brazil (by CONAMA) and USA (by USEPA), the maximum concentration of the total oils and grease (TOG) in effluent disposal in the seabed is 29mg/L (29ppm) in a monthly average, and 42mg/L (42ppm) the daily maximum (CON)(Clark, et al., 2009). For inland resources, the restrictions can be even tighter as water are less diluted.

Oily wastewater from oil and gas production – the produced water - receives a noteworthy attention due to their large production volumes, its physic-chemical particularities, and the substantial economic impact in the industry.

2.8.1. Produced water

Produced water (PW) is the conventional name given to water from underground formations that reach the surface in oil or gas production. This water is permeated in naturally occurring porous rocks in subsurface formations together with petroleum (solid, liquid and gas) which is trapped by impermeable rocks. Produced water can comprise "formation water" which is the naturally occurring water in the underground formation and "injected water" that contains injected fluids and additives originated from drilling and production activities, like enhancing oil recovery (EOR). Produced water is not a single commodity. It contains some of the characteristics of the formation from which it was storage for thousands of years, possible chemicals additives dosed during industrial processes and associated hydrocarbon. Moreover, its properties and composition can change through the life time of the reservoir (Clark, et al., 2009)(Veil, et al., 2004). The complex composition frequently includes organic and inorganic substances, with the main components being salts, free and emulsified oils, phenols, organic acids, benzene, toluene, ethyl benzene, xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs). Among these components, the oil and grease fraction is the one with more legislative restrictions for discharge (Jiménez, et al., 2017). This oil is present in different forms: besides the dissolved hydrocarbon, it is found in droplets with diameter larger than 150microns – that can be separated by conventional methods (except for heavy oil); particle between 15-150 micron (free droplets); and stabilized oil in water emulsion, with the median droplet diameter usually in the range of 3-20 micron (Moosal, et al., 2002). Table 4 presents the main components of a PW.

Table 4: Main components of produced water from oilfields (Jiménez, et al., 2017).

Compound group	Concentration mg/L
Salts	Up to 300000
Oil and grease	15-200
BTEX	0.7-24
PAH	0.04-3
Organic Acids	7-760
Phenols	0.4-23

Produced water is generated in large amounts. In literature it has been found a wide oil to water proportions such as 1:2,8 (2016) 1:3 (Jiménez, et al., 2017), 1:5-7 (Rawlins, 2011) and even up to 1:10 (Atarah, 2011) for cases of mature fields. Water volumes in any reservoir increase as the oil and gas field reaches maturity. In addition to that, (produced)water can be (re)injected to maintain reservoir pressure and hydraulically drive oil toward a production well – practice often referred as enhanced oil recovery (EOR) or water flooding or steam flood, depending upon the temperature of the water (Clark, et al., 2009). In this practice of injection, water can dilute the formation water and affect the produced volume. Figure 16 presents worldwide PW production per day (onshore and offshore). It shows a daily production of around 300 million barrels during 2013-2015, which corresponds to around 50 millionm^3 per day (each barrel is 0.159 m^3). Reports of world oil production point to an approximately 90 million barrels per day in 2016 (BPS17), as shown on Figure 21. This corresponds to 14,3 million m^3/day of oil. The importance of produced water is such that its volume is often the limiting factor for sizing the entire production system (Rawlins, 2009).

As just mentioned, the produced water can be reinjected into wells for EOR purposes and/or as a discharge alternative. This is done for most of PW generated in offshore facilities. The PW can also be discharged in hydric systems, which is the case of onshore units. In both cases, respectively to avoid plugging in the well and to comply with the legislation that impose discharge limits, the produced water has to fulfil required specifications.

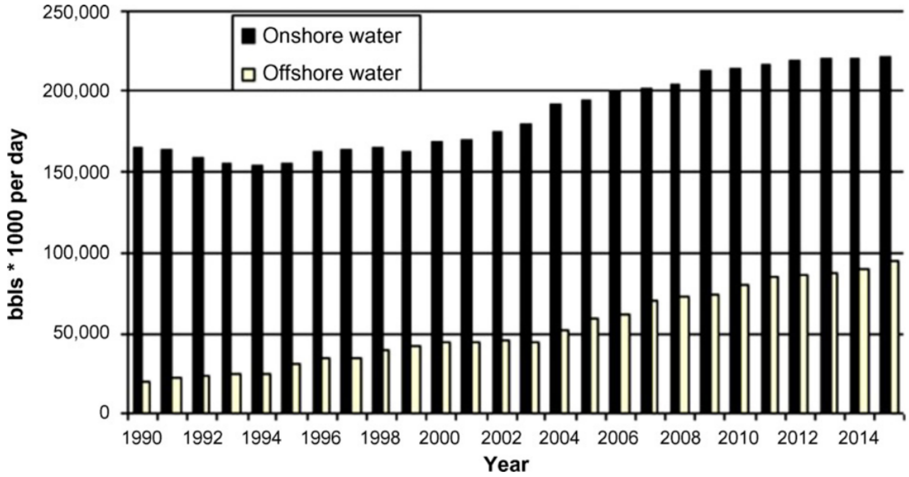


Figure 20: Global onshore and offshore water production. Source: (Ahmadun, et al., 2009)

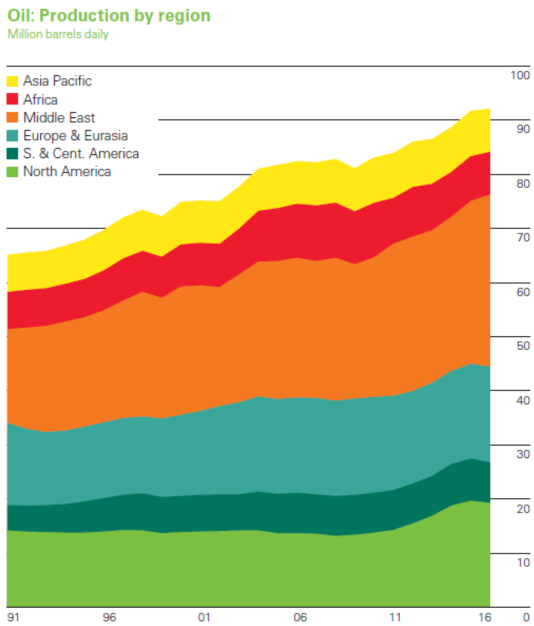


Figure 21: Oil production per year in million barrels per day. Source: (BPS17)

In addition to comply with process and governmental requirements, recovery of the oil from PW also contributes to financial gains. According to Rawlins (Rawlins, 2009) estimation, considering an oil price of $50 per barrel, a barrel of PW containing one hundred parts per million (volume base) has $0,21 of oil. In large scales it may represents significant volumes. Figure 22 presents the discharged oil from produced water in the United Kingdom (ENV16) and gives an idea of the amount of oil lost/discharged together with the produced water.

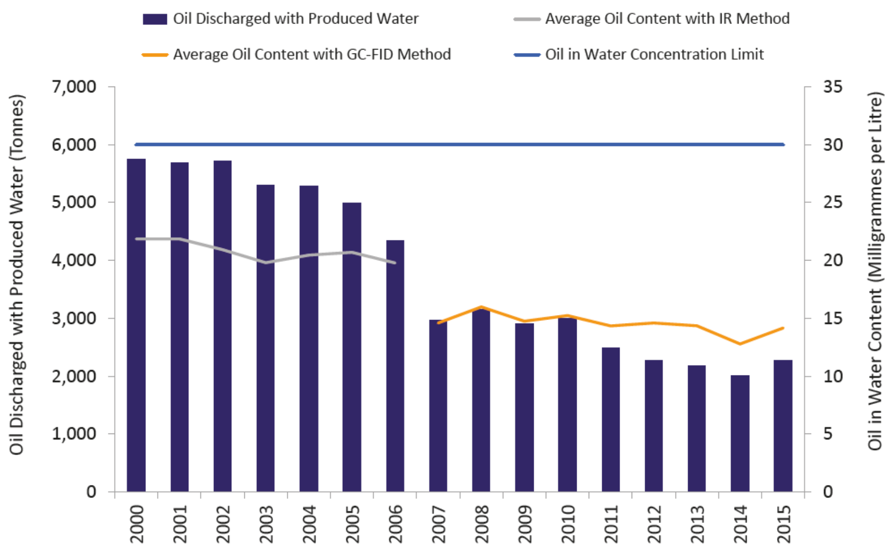


Figure 22: Oil discharged with produced water to sea in UK (see *note below). Source: (ENV16)

***Note**: Up to 2006, oil concentration in produced water was measured using the infrared method (IR). The IR method measures, in solvent, both the dispersed and dissolved hydrocarbons extracted. This method can, however, include other organic chemicals, giving an artificially high result and can also underestimate dissolved hydrocarbons. To rectify this and to provide a more accurate analysis of hydrocarbon content, OSPAR agreed (Agreement 2005-15) the use of a new method for oil in water analyses, based on a modified version of the ISO 9377-2 (GC-FID) method(ENV16).

In the oil and gas production, for the separation of each phase the fluid passes through different separation processes as gravitational separation vessels (2 or 3 phase separators), desanders (solid removal) and dehydrator/coalescers (oil treatment). The produced water treatment system collects and combine all water streams and treats them for appropriate disposal. The PW system commonly comprises an initial stage for big oil droplets removal – the hydrocyclones and fallowed by flotation system for fine droplets removal. An extra stage of deep bed media (as walnut and pecan shell) filtration can be applied to some cases. In onshore units and fixed platforms, mechanical type of IGF have found significant use as these facilities are not motion and space sensitive. For offshore applications, more compact units within the IGF and DGF are preferred (Rawlins, 2009).

2.9. Simulation and control

Better understanding and/or improvements of the flotation unit design and process operation can be achieved by means of simulation and control. Works related to mix modeling and steady state control contribute to process optimization and help to handle operation issues.

The turbulent flow from the mixing region, characterized in terms of the energy dissipation per water volume (contact zone), promotes the collision between particles and bubble when properly adjusted. It also may cause detachments if overestimated. Therefore, the understanding of the process hydrodynamic is very important. Computational fluid dynamics (CFD) is a valuable tool in this regard. In CFD modeling, the flotation unit is discretized into individual finite volumes where local values of flow properties are calculated, i.e., it provides local turbulent dissipation rates/collision rates within any part of the flotation cell. The detailed understanding of flow using this approach allows performance improvement and optimize equipment design. (Edzwald, et al., 2011)(KOH, et al., 2006).

Besides gains in hydrodynamics, simulation also brings benefits by assisting the control. Bouchard, *et al*. (2009) highlight three areas within the flotation (column) modeling in the process control: recovery prediction, analysis of dynamic behavior, and development of soft sensors to improve instrumentation for flotation. According to their report, the control objectives follow the fallowing hierarchy level: 1) keep a steady operation – by damping feedings disturbances as much as possible, 2) stabilizing control – by keeping the process variables with strong process influence in a bounded region, i.e. an acceptable operating zone where it is possible to handle the process and reach production objective, including safety, and 3) optimizing control – by establishing set-points to drive the process into targets criteria in order to achieve the economic objective.

These are artifices that, among others, contribute for the flotation process development. It is valid to point out that caution is needed with the reliability of the instrumentation and control systems, and careful interpretation of the simulated results is required due to challenges in modeling three-phase flow (water, particles and bubbles).

2.10. Technological prospection

The technological prospection, also called forecast(ing), foresight(ing) or future studies, as per the definition of Borschiver, *et al*. (2016), is a set of concepts and techniques applied to foresee the behavior of variables such as socio-economic, political, cultural and technological as well as the effects of their interactions. The study can aid the technology identification that may be of interest of an organization, and point to possible business and partnership. This is a useful method for the evaluation of further consequences of current optional actions. Therefore, it is a functional tool for corporation planning, as well as for sectoral and public politics.

The technological prospection can enclose an extensive outlook as in a wide universe where a significant number of parameters, variables and players are involved and have to be evaluated, or in a more restricted window as for per specific studies for corporations comprising limited factors. Likewise, the complexity can be restricted for instance to the evaluation of one technology for a single institution, or multiple subjects within different economic sectors or even comprising an entire society. By making use of such study, the companies aim to identify the factors degree of influence in their products and business. The evaluation of relevant information organized and interpreted systematically contributes significantly in a decision-making process. Evidently, corporate decisions with regards technologies shall be managed considering additional aspects like their business strategy.

Numerals methodologies can be applied in the foresight study. It can encompass interviews and brainstorming and be upheld by scenarios set. It can make use of the SWOT analysis (Strength, Weakness, Opportunity and Threaten evaluation), the Delphi method (considers contribution of experts), the cross-impact technique (simulation of events cause relations), the data mining (further correlations studies) and the trend analysis that is based on the assumptions that past behaviors will be maintained in the future. A supplementary technique is the technology roadmapping (TRM) that contemplates corporates considerations and support management planning (Borschiver, et al., 2016).

In addition to help in the corporate managing, foresight can come up with valuable information for professionals in correlated areas as the ones from the R&D area. The knowledge on the historical usage, trends and the relation among factors can be useful complementary information for academic matters.

Technology prospection is a challenging and not easy work due to its interdisciplinary, wide-ranging, and complex profile that requires elaborated analysis and creativity to develop the forecast. Because of this dynamic, each analyzer team may come up with a particular output. In this work it was opted to perform the technologic prospection of the gas flotation process in the application of the oily water treatment by evaluating the latest developments in the academic and industrial sector, i.e., by means of scientific papers and patents.

3. TECHNOLOGICAL PROSPECTION METHODOLOGY

3.1. General methodology

The patent and scientific papers analysis were made by using the Technological Prospection methodology developed by the *Núcleo de Estudos Industriais e Tecnológico*s (NEITEC) (Technologic and Industrial Study Center) of *Escola de Química - Universidade Federal do Rio de Janeiro (UFRJ)*, in which keywords direct the documents search. The search results are then listed, filtered and detailed according to the chosen focus. The study was based on Macro, Meso and Micro analysis as below:

- Macro analysis: the information are organized and set according to the following criteria: time series (2010 until 07/2017), country and affiliation (for papers) or assignee (patents) sorted by university, institute and company.
- Meso analysis: the document content is organized and analyzed according to the chosen taxonomies, taking into consideration the observed tendencies in the content. It is important to highlight that these taxonomies can change from papers to patents and that they cannot be previously set once they depend on their content, i. e., the documents have to be read beforehand. Moreover, one document can present more than one taxonomy.
- Micro analysis: description of the taxonomies considered on the Meso analysis, with the possibility to add more items to be evaluated, in case a more detailed examination is needed.

Before describing the methodology, it is interesting to define the objects of the study in this work - scientific paper and patents. The description of each one was taken from respected bodies and are presented below:

Scientific Paper description by the Journal Nature (Nat17):

"Scientific papers are for sharing your own original research work with other scientists or for reviewing the research conducted by others. As such, they are critical to the evolution of modern science, in which the work of one scientist builds upon that of others. To reach their goal, papers must aim to inform, not impress. They must be highly readable — that is, clear, accurate, and concise. They are more likely to be cited by other scientists if they are helpful rather than cryptic or self-centered."

Patent description by WIPO- World Intellectual Property Organization (WIP17):

"A patent is an exclusive right granted for an invention, which is a product or a process that provides, in general, a new way of doing something, or offers a new technical solution to a problem. To get a patent, technical information about the invention must be disclosed to the public in a patent application."

3.2. Search methodology – Papers

Two databases were considered for this study: Science Direct and Scopus.

Science Direct is a website launched in 1997 and operated by the publisher Elsevier. It is a platform that provides access to a large database of scientific, technical, and medical research. It hosts over 12 million pieces of content from 3,500 academic journals and 34,000 e-books. Its article abstracts are freely available, but access to their full texts generally require a subscription or purchase. Elsevier also owns **Scopus**. Similarly, it is a bibliographic database available online upon subscription. It contains abstracts and citations for academic journal articles covering nearly 22,000 titles from over 5,000 publishers, of which 20,000 are peer-reviewed journals in different fields of sciences (Els17).

Based on the available resources in UFRJ with regards papers research, it was initially chosen Science Direct for the papers database for this study, since it gives full access to the papers. However, a second database was considered afterwards as a way of increasing the number of papers to be analyzed, as the selection on Science Direct did not give satisfactory quantity. This will be presented in the results section.

This second database is Scopus. It may give more results for some researches (including some of Science Direct), but not all papers are fully accessible, i.e., only the summary was available for many papers. It was noted that the papers with access to the entire content tracked in Scopus were also in the Science Direct results.

3.2.1. Search tool and criteria

3.2.1.1. Science direct

On Science Direct website, it was chosen the option “Advanced search”. In the available tool, shown in Figure 23, two keywords were selects together with their location in the paper, for example location at <Title> or <Abstract, Title, Keyword>.

For this work the first keyword was always the word <flotation>, and the second keyword was always considered with the logic <AND>, i.e., selecting only publications that consider both criteria. The variations for the search were the second keywords and the location of both keywords.

All searches considered the default publication source, i.e., journals, books and reference work from all sciences. The selected years were from 2010 to present (2017).

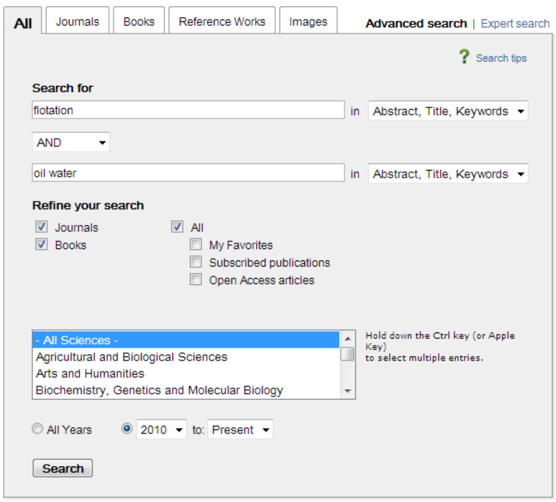


Figure 23: “Advanced search” tool on Science Direct website

The character quotation mark <”> was used to restrict the search for word(s) exactly as it is written. For instance, the search for “oil water” will only consider publication with this both words together. So, “oily water” will not be considered.

The character asterisks < * > was used to replace any possible letter(s) on that exactly word. For example, the search of “oil* water” will consider as results “oil water”, “oily water”, etc.

3.2.1.1. Scopus

Similar philosophy was followed for Scopus search. The document search tool from this data base can be seen on Figure 24 bellow. It is more versatile than the Science Direct search tool. In this tool it is possible to add extras lines by clicking in the "+" symbol in the right side, it gives a wider combination of keywords and its location. It was not used in the research though, because the location of the second and third keywords were always in the <Abstract, Title, Keyword> and the logic/word "AND" was enough for the combination of them.

It was select the year range from 2010 to present (2017) and the results restricted to article and reviews.

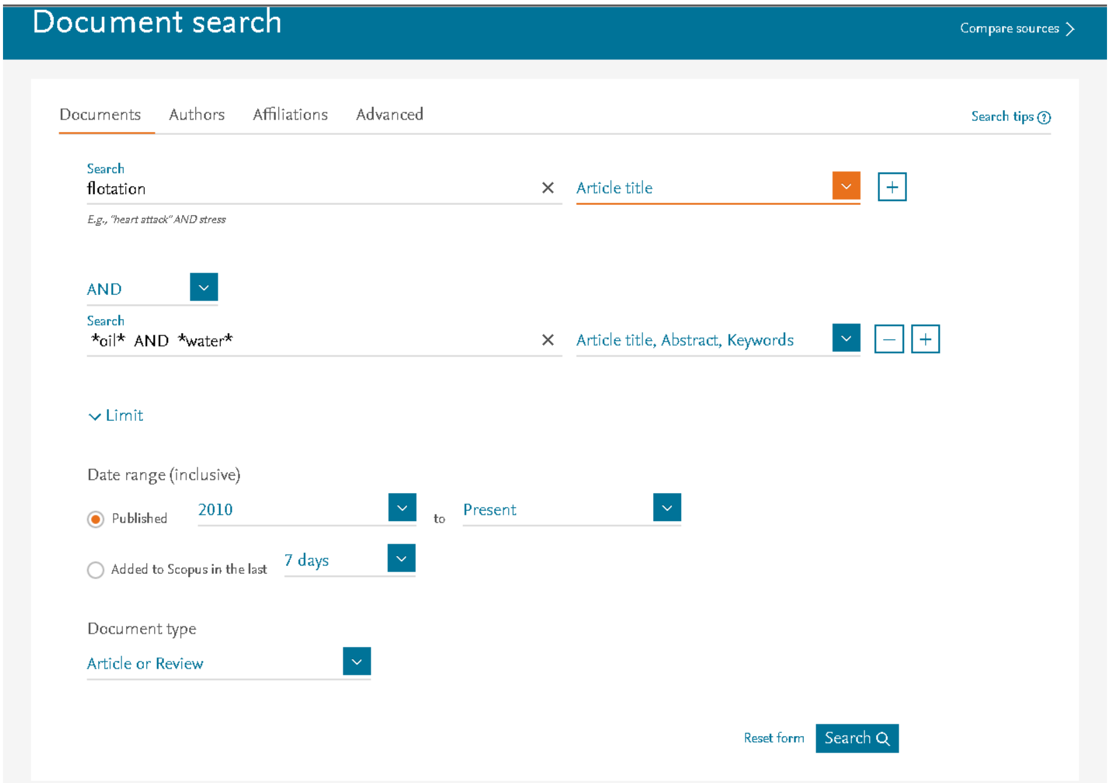


Figure 24: Documents search tool on Scopus web site

3.2.2. Search results for papers

A screen print from the Science Direct and Scopus result page can be seen on Figure 25 and on Figure 26, respectively. They have similar output layout. On the top of the page it shows the papers quantity together with a summary of the search criteria. Bellow this, it can be found the papers list. On the left side, it is shown a summary of some classifications as year, publication title, etc. This left side information was selected, copied and pasted in Excel for data analysis. A more detailed summary can also be achieved by using the “Export” button above the papers list. Similarly, the excel was used for data evaluation and chart construction.

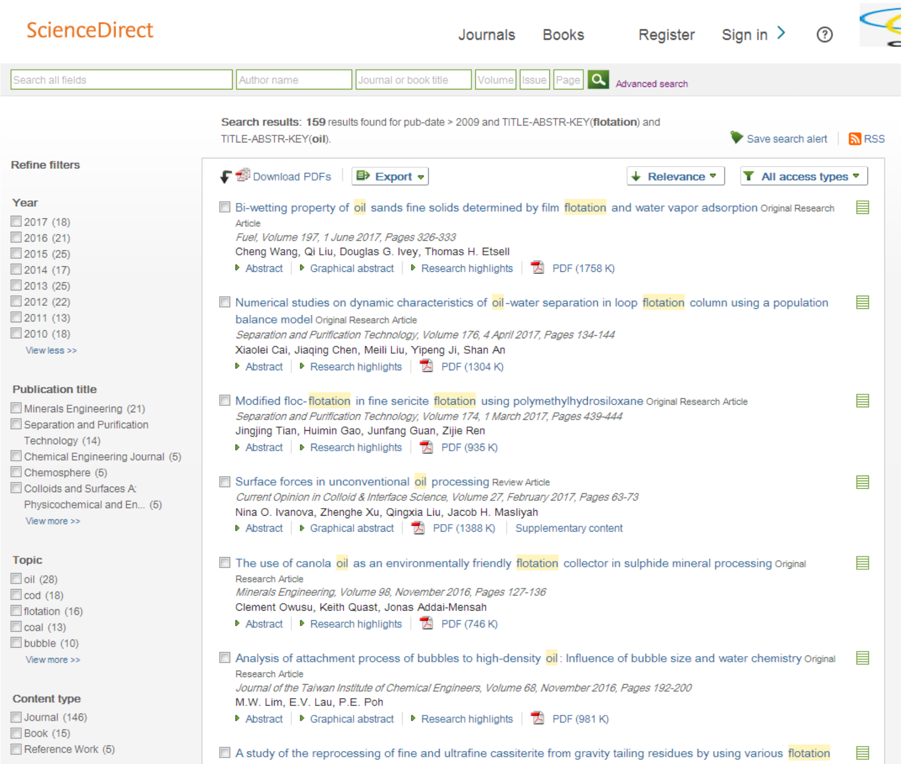


Figure 25: Screen print of result page from Science Direct search

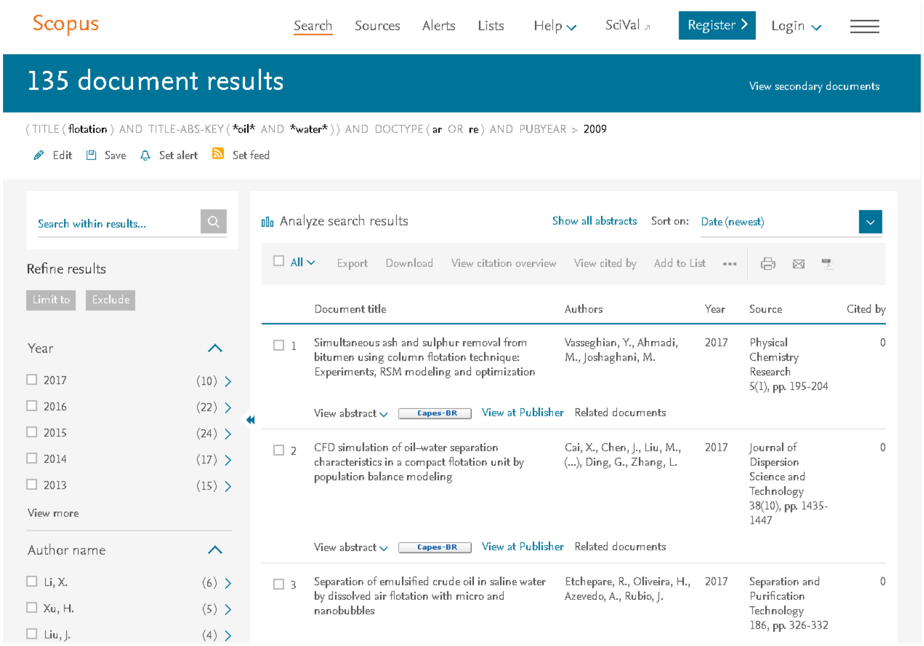


Figure 26: Screen print of result page from Scopus search

3.3. Search methodology – Patents

In order to have the picture of Brazil and also the international scenario, two databases were considered for this study: USPTO and INPI.

USPTO is the acronym for the United States Patent and Trademark Office. It is a federal agency of the U.S. Department of Commerce that grants U.S. patents and register trade marks for the protection of inventions. The agency examines applications and determine the invention entitlement. The issued patents are available for public use. U.S. patent grants are effective only within the United States territories and possessions (USP17). Created on 1970, **INPI** is the Brazilian national institute for industrial property (*Instituto Nacional da Propriedade Industrial*). It is a federal institution linked to the Ministry of Industry, Foreign Trade and Service. Like the USPTO, INPI is responsible for the Brazilian intellectual property entitlement, and its patents is valid in Brazil (INP17).

3.3.1. Search tool and criteria

3.3.1.1. USPTO

On USPTO website, it was chosen the option “Searching Full Text Patents” - “Advanced search”. In the available tool, shown in Figure 27, it was given specifications of time range and keywords, following the same logic of the papers. On the Query box shown in the figure, the stipulations are set by typing the field codes followed with the desired specifications. In this work only three codes were used to the search: “Title” which field code is TTL, “Abstract” which field code is ABST and Issued day which field code is ISD. For example: <TTL/Flotation> will search patents that have the word <flotation> on the title, and ISD/20100101->20170710 will search patents within the date range of 1st January of 2010 till 10th July of 2017. Additional terms can be added by using “AND”, “OR” and “ANDNOT” operators.

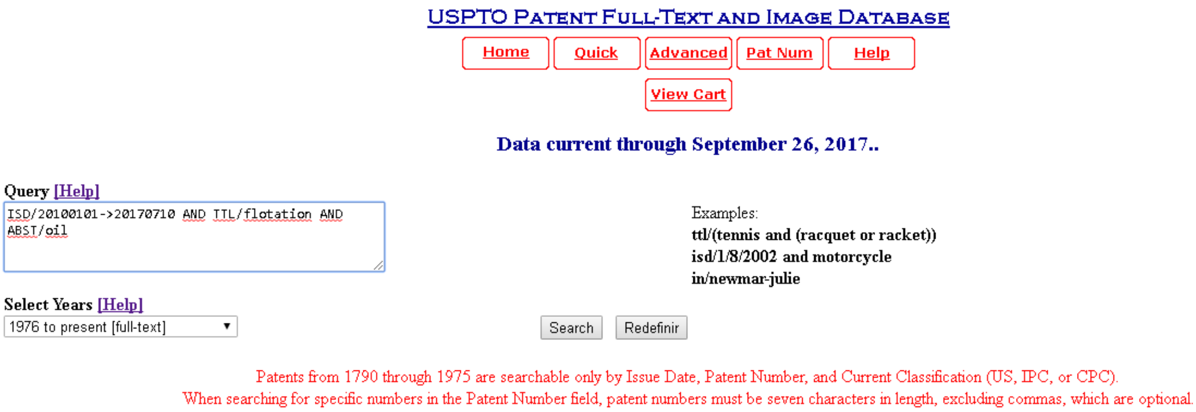


Figure 27: “Advanced search” tool USPTO website

3.3.1.2. INPI

The patents search tool from INPI is more user-friendly and it shows the available fields for search. It is necessary to input the specification in each field, as can be seen on Figure 28. The search philosophy applied was the same.

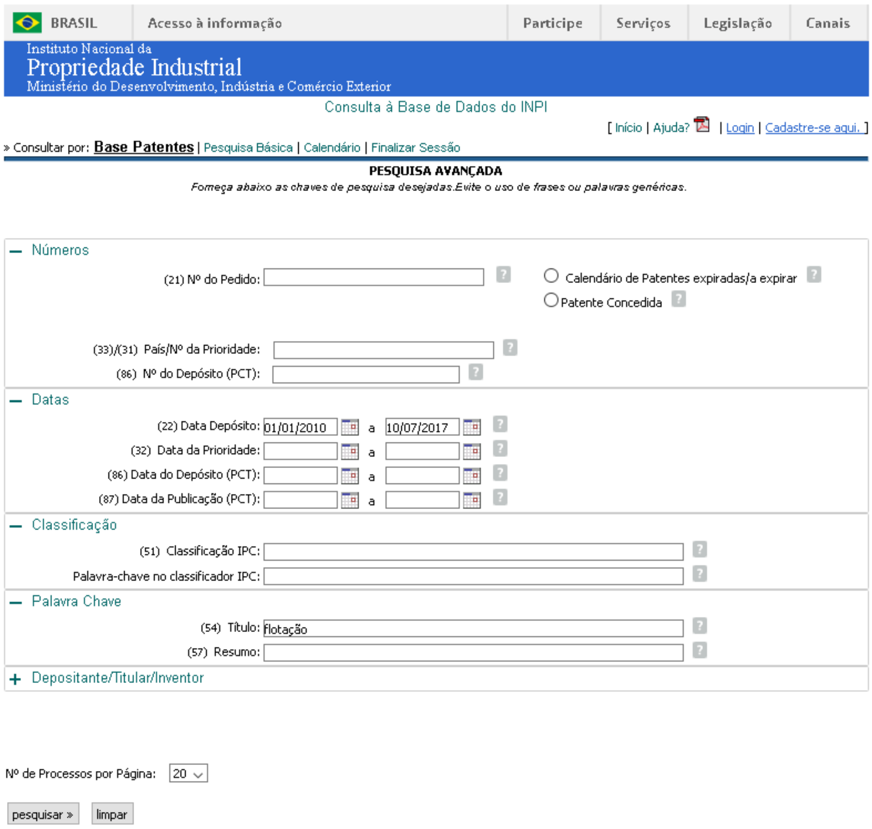


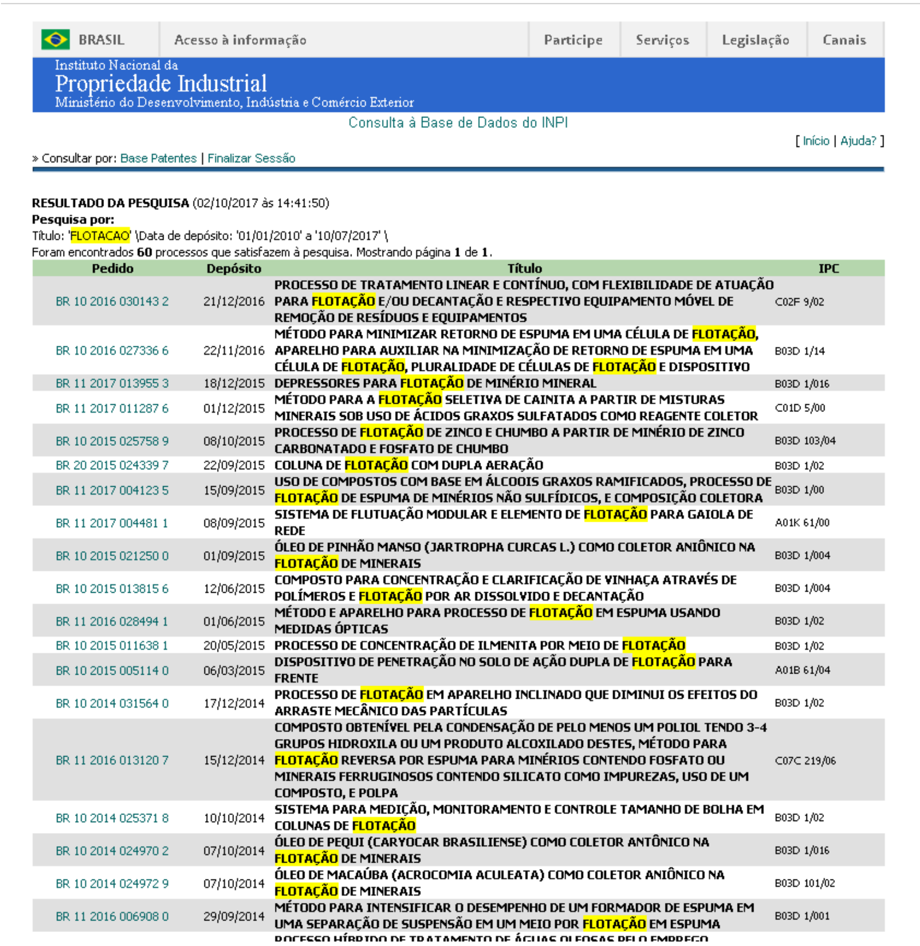
Figure 28: Patent search tool on INPI site

3.3.2. Search results for Patents

A screen print from the SCOPUS and INPU result page can be seen on Figure 29 and on Figure 30, respectively. None of them have an option to export/download a summary data, as there were on the papers. The INPI result´s page shows the patent number, date, title and IPC number – that is the International Patent Classification that provides information about the area of technology to which the patents pertain. The USPTO result´s page provides solely the patent number and title.

The patents had to be access by opening one by one. They were all copied into an excel file and by means of functions a list with basic data were set. This list served as the base of the evaluation and selection of the applicable documents.

Figure 29: Screen print of result page from USPTO search



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Instituto Nacional da
Propriedade Industrial
Ministério do Desenvolvimento, Indústria e Comércio Exterior

Consulta à Base de Dados do INPI

[Início | Ajuda?]

» Consultar por: Base Patentes | Finalizar Sessão

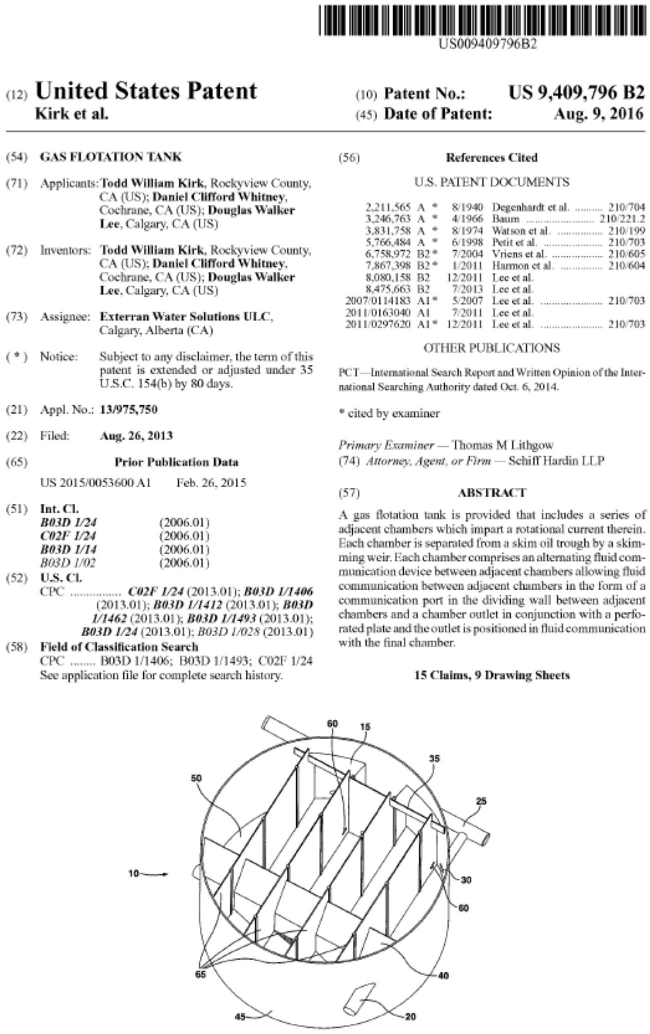
RESULTADO DA PESQUISA (02/10/2017 às 14:41:50)
Pesquisa por:
Título: 'FLOTACAO' \Data de depósito: '01/01/2010' a '10/07/2017' \
Foram encontrados **60** processos que satisfazem à pesquisa. Mostrando página **1** de **1**.

Pedido	Depósito	Título	IPC
BR 10 2016 030143 2	21/12/2016	PROCESSO DE TRATAMENTO LINEAR E CONTÍNUO, COM FLEXIBILIDADE DE ATUAÇÃO PARA FLOTAÇÃO E/OU DECANTAÇÃO E RESPECTIVO EQUIPAMENTO MÓVEL DE REMOÇÃO DE RESÍDUOS E EQUIPAMENTOS	C02F 9/02
BR 10 2016 027336 6	22/11/2016	MÉTODO PARA MINIMIZAR RETORNO DE ESPUMA EM UMA CÉLULA DE FLOTAÇÃO, APARELHO PARA AUXILIAR NA MINIMIZAÇÃO DE RETORNO DE ESPUMA EM UMA CÉLULA DE FLOTAÇÃO, PLURALIDADE DE CÉLULAS DE FLOTAÇÃO E DISPOSITIVO	B03D 1/14
BR 11 2017 013955 3	18/12/2015	DEPRESSORES PARA FLOTAÇÃO DE MINÉRIO MINERAL	B03D 1/016
BR 11 2017 011287 6	01/12/2015	MÉTODO PARA A FLOTAÇÃO SELETIVA DE CAINITA A PARTIR DE MISTURAS MINERAIS SOB USO DE ÁCIDOS GRAXOS SULFATADOS COMO REAGENTE COLETOR	C01D 5/00
BR 10 2015 025758 9	08/10/2015	PROCESSO DE FLOTAÇÃO DE ZINCO E CHUMBO A PARTIR DE MINÉRIO DE ZINCO CARBONATADO E FOSFATO DE CHUMBO	B03D 103/04
BR 20 2015 024339 7	22/09/2015	COLUNA DE FLOTAÇÃO COM DUPLA AERAÇÃO	B03D 1/02
BR 11 2017 004123 5	15/09/2015	USO DE COMPOSTOS COM BASE EM ÁLCOOIS GRAXOS RAMIFICADOS, PROCESSO DE FLOTAÇÃO DE ESPUMA DE MINÉRIOS NÃO SULFÍDICOS, E COMPOSIÇÃO COLETORA	B03D 1/00
BR 11 2017 004481 1	08/09/2015	SISTEMA DE FLUTUAÇÃO MODULAR E ELEMENTO DE FLOTAÇÃO PARA GAIOLA DE REDE	A01K 61/00
BR 10 2015 021250 0	01/09/2015	ÓLEO DE PINHÃO MANSO (JARTROPHA CURCAS L.) COMO COLETOR ANIÔNICO NA FLOTAÇÃO DE MINERAIS	B03D 1/004
BR 10 2015 013815 6	12/06/2015	COMPOSTO PARA CONCENTRAÇÃO E CLARIFICAÇÃO DE VINHAÇA ATRAVÉS DE POLÍMEROS E FLOTAÇÃO POR AR DISSOLVIDO E DECANTAÇÃO	B03D 1/004
BR 11 2016 028494 1	01/06/2015	MÉTODO E APARELHO PARA PROCESSO DE FLOTAÇÃO EM ESPUMA USANDO MEDIDAS ÓPTICAS	B03D 1/02
BR 10 2015 011638 1	20/05/2015	PROCESSO DE CONCENTRAÇÃO DE ILMENITA POR MEIO DE FLOTAÇÃO	B03D 1/02
BR 10 2015 005114 0	06/03/2015	DISPOSITIVO DE PENETRAÇÃO NO SOLO DE AÇÃO DUPLA DE FLOTAÇÃO PARA FRENTE	A01B 61/04
BR 10 2014 031564 0	17/12/2014	PROCESSO DE FLOTAÇÃO EM APARELHO INCLINADO QUE DIMINUI OS EFEITOS DO ARRASTE MECÂNICO DAS PARTÍCULAS	B03D 1/02
BR 11 2016 013120 7	15/12/2014	COMPOSTO OBTENÍVEL PELA CONDENSAÇÃO DE PELO MENOS UM POLIOL TENDO 3-4 GRUPOS HIDROXILA OU UM PRODUTO ALCOXILADO DESTES, MÉTODO PARA FLOTAÇÃO REVERSA POR ESPUMA PARA MINÉRIOS CONTENDO FOSFATO OU MINERAIS FERRUGINOSOS CONTENDO SILICATO COMO IMPUREZAS, USO DE UM COMPOSTO, E POLPA	C07C 219/06
BR 10 2014 025371 8	10/10/2014	SISTEMA PARA MEDIÇÃO, MONITORAMENTO E CONTROLE TAMANHO DE BOLHA EM COLUNAS DE FLOTAÇÃO	B03D 1/02
BR 10 2014 024970 2	07/10/2014	ÓLEO DE PEQUI (CARYOCAR BRASILIENSE) COMO COLETOR ANTÔNICO NA FLOTAÇÃO DE MINERAIS	B03D 1/016
BR 10 2014 024972 9	07/10/2014	ÓLEO DE MACAÚBA (ACROCOMIA ACULEATA) COMO COLETOR ANIÔNICO NA FLOTAÇÃO DE MINERAIS	B03D 101/02
BR 11 2016 006908 0	29/09/2014	MÉTODO PARA INTENSIFICAR O DESEMPENHO DE UM FORMADOR DE ESPUMA EM UMA SEPARAÇÃO DE SUSPENSÃO EM UM MEIO POR FLOTAÇÃO EM ESPUMA	B03D 1/001

Figure 30: Screen print of result page from INPI search

Each base has its own patents standard layout with the main information shown on the front page as inventors, dates, summary and sometimes a drawing. Figure 31 and Figure 32 show respectively the patents profile from USPTO and from INPI. As can be observed USPTO shows more information on its front page.

It is important to mention that all patents found in the USPTO base had linked a pdf document that could be download, and all the fields where filled, while in the INPI base most of patents did not have a file, and some patents did not have basic information as the abstract.



US009409796B2

(12) **United States Patent**
Kirk et al.

(10) **Patent No.:** **US 9,409,796 B2**
(45) **Date of Patent:** **Aug. 9, 2016**

(54) **GAS FLOTATION TANK**

(71) Applicants: **Todd William Kirk**, Rockyview County, CA (US); **Daniel Clifford Whitney**, Cochrane, CA (US); **Douglas Walker Lee**, Calgary, CA (US)

(72) Inventors: **Todd William Kirk**, Rockyview County, CA (US); **Daniel Clifford Whitney**, Cochrane, CA (US); **Douglas Walker Lee**, Calgary, CA (US)

(73) Assignee: **Exterran Water Solutions ULC**, Calgary, Alberta (CA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 80 days.

(21) Appl. No.: **13/975,750**

(22) Filed: **Aug. 26, 2013**

(65) **Prior Publication Data**

US 2015/0053600 A1 Feb. 26, 2015

(51) **Int. Cl.**

B03D 1/24	(2006.01)
C02F 1/24	(2006.01)
B03D 1/14	(2006.01)
B03D 1/02	(2006.01)

(52) **U.S. Cl.**
CPC ***C02F 1/24*** (2013.01); ***B03D 1/1406*** (2013.01); ***B03D 1/1412*** (2013.01); ***B03D 1/1462*** (2013.01); ***B03D 1/1493*** (2013.01); ***B03D 1/24*** (2013.01); *B03D 1/028* (2013.01)

(58) **Field of Classification Search**
CPC B03D 1/1406; B03D 1/1493; C02F 1/24
See application file for complete search history.

(56) **References Cited**

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3,246,763	A *	4/1966	Baum	210/221.2
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* cited by examiner

Primary Examiner — Thomas M Lithgow
(74) *Attorney, Agent, or Firm* — Schiff Hardin LLP

(57) **ABSTRACT**

A gas flotation tank is provided that includes a series of adjacent chambers which impart a rotational current therein. Each chamber is separated from a skim oil trough by a skimming weir. Each chamber comprises an alternating fluid communication device between adjacent chambers allowing fluid communication between adjacent chambers in the form of a communication port in the dividing wall between adjacent chambers and a chamber outlet in conjunction with a perforated plate and the outlet is positioned in fluid communication with the final chamber.

15 Claims, 9 Drawing Sheets

Figure 31: Example of USPTO Patent

República Federativa do Brasil
Ministério da Indústria, Comércio Exterior e Serviços
Instituto Nacional da Propriedade Industrial

(21) BR 102014024143-4 A2

(22) **Data do Depósito:** 29/09/2014

(43) **Data da Publicação:** 08/11/2016

(54) Título: ROCESSO HÍBRIDO DE TRATAMENTO DE ÁGUAS OLEOSAS PELO EMPREGO SIMULTÂNEO DE CÂMARAS DE FLOTAÇÃO E ÁREA ALAGADA CONSTRUÍDA POVOADA POR MACRÓFITAS FLUTUANTES

(51) Int. Cl.: C02F 9/14; C02F 1/24; C02F 3/32; C02F 101/32

(73) Titular(es): CENTRO DE GESTÃO DE TECNOLOGIA E INOVAÇÃO - CGTI

(72) Inventor(es): VALDEMIR ALEXANDRE DOS SANTOS, LEONIE ASFORA SARUBBO, ALEX ELTON MOURA, RAQUEL DINIZ RUFINO, JULIANA MOURA DE LUNA

(57) Resumo: PROCESSO HÍBRIDO DE TRATAMENTO DE ÁGUAS OLEOSAS PELO EMPREGO SIMULTÂNEO DE CÂMARAS DE FLOTAÇÃO E ÁREA ALAGADA CONSTRUÍDA POVOADA POR MACRÓFITAS FLUTUANTES. A presente invenção, que pertence a área de engenharia sanitária, e mais especificamente de tratamento de águas, refere-se a um processo de tratamento de afluente (1) composto por águas oleosas, constituído de duas etapas: tratamento inicial pelo processo de flotação, seguido pelo processo biológico utilizando o tratamento por área alagada construída (4) , povoada com macrófitas flutuantes (20) da espécie Eichhornia crassipes; o referido processo possui produção reduzida de resíduos e permite, além da recuperação do óleo residual, a produção de água de reuso, com opção de retorno aos recursos hídricos localizados nas proximidades do entorno das instalações do sistema de tratamento.

Figure 32: Example of INPI Patent

4. RESULTS FROM THE PAPERS TECHNOLOGICAL PROSPECTION

The results from the technological prospection and their evaluations are presented below in the following order: first Papers and second Patents.

In order to distinguish the keyword(s) that considered the quotation mark character (“) from the ones that did not considered it, all keyword(s) will be presented between arrows as: <”oil water”> and <oil water>.

The general results from different searches in Science Direct database from 2010 and 2017 is shown on Table 5. It gives an overview of the publications quantity related to the flotation considering a diverse combination of keywords and its location.

It was found 1140 papers containing the word <flotation> in the title. Almost double of it (2316) is acquired when besides the title, the abstract and keywords are additionally considered.

Table 5: Search results from Science Direct on 27-May-2017.

Item name	Keyword 1	Location of keyword 1	(AND) Keyword 2	Location keyword 2	Results
Item 1 - flot. @Abst (2316)	flotation	Abstract, Title, keywords	-	-	2316
Item 2 - flot. @Title (1140)	flotation	Title	-	-	1140
Item 3 - @Abst & oil (159)	flotation	Abstract, Title, keywords	oil	Abstract, Title, keywords	159
Item 4 - @Abst & oil water (75)	flotation	Abstract, Title, keywords	oil water	Abstract, Title, keywords	75
Item 5 - @Abst & "oil* water" (13)	flotation	Abstract, Title, keywords	"oil* water"	Abstract, Title, keywords	13
Item 6 - @Abst & "produced water" (11)	flotation	Abstract, Title, keywords	"produced water"	Abstract, Title, keywords	11
Item 7 -@Tit & oil (82)	flotation	Title	oil	Abstract, Title, keywords	82
Item 8 -@Tit & "oil* water" (9)	flotation	Title	"oil* water"	Abstract, Title, keywords	9
Item 9 - @Tit & oil water (41)	flotation	Title	oil water	Abstract, Title, keywords	41
Item 10 - @Tit & "produced water" (7)	flotation	Title	"produced water"	Abstract, Title, keywords	7

Figure 33 shows the historical publications of papers on the last years, with 2017 comprising partial months. An initial overall evaluation can be done from these data. It is noticed an increase trend on the number of papers related to the flotation process in general (Items 1 and 2 from Table 5), which indicates a growth on the research efforts related to flotation process in general.

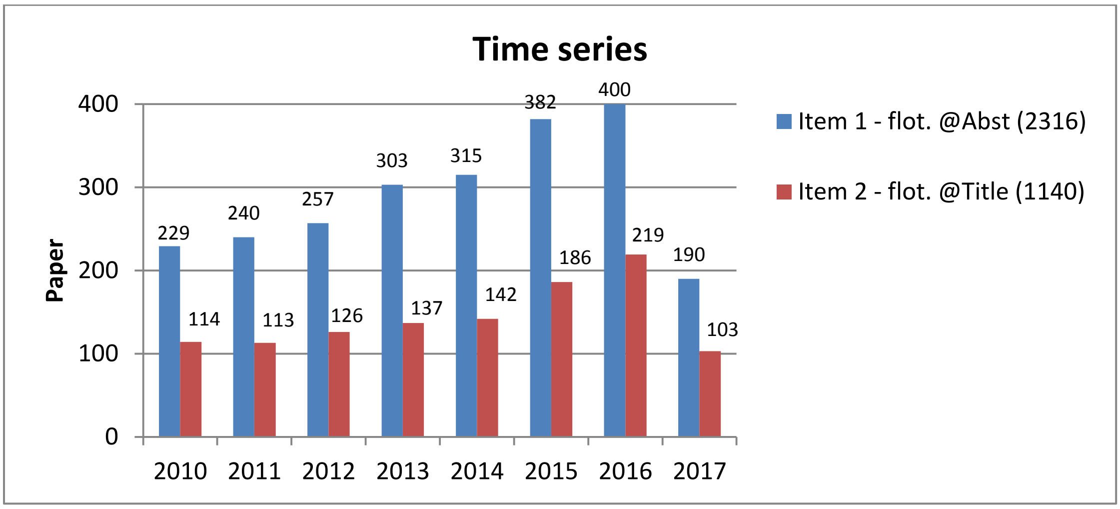


Figure 33: Quantity of papers published per year for Items 1 and 2 base on Science Direct

From the 1140 papers containing <flotation> in the title (item 2), only 82 mention the word <oil> in the abstract (item 7 from Table 5), and from this group just 41 mention <water> as well (item 9 from Table 5). This first evaluation was an initial indication that oily water treatment was not the focus from the research related to flotation process made by the papers. By analyzing the journals related with these same publications (item 2 from Table 5), it was found mineral related journals as majority source, as can be observed on Table 6. Both analysis agree and corroborate the literature report that mining is the main field of study from flotation related papers published in the last years.

Table 6: Journals name in decrease order from Item 2 - flot. @Title (1140)

Rank	Journal	Papers
1	Minerals Engineering	405
2	International Journal of Mineral Processing	139
3	Separation and Purification Technology	55
4	Powder Technology	46
5	Transactions of Nonferrous Metals Society of Ch...	36
	Others	459

In this study, it was assumed that the papers comprising <flotation> in the title are the ones more likely to focus the research on the flotation process itself, and the rest (<flotation> in abstract and keywords) as less prone to that, possibly just mentioning this process as adjacent phenomena with secondary aim. The ones considering <oil> in the title, abstract and keywords were considered as more probable to be from the Oil & Gas application, which is the field of interest of this study. Therefore, item 7 (@Tit & oil (82)) from Table 5 (highlighted with red rectangle) was chosen as the paper source list for selecting the publications.

It should be noticed from Table 5 that the item 9 (@Tit & oil water (41)) is a subgroup of item 7, which in addition to <oil> the word <water> is also present. This item 9 would have being a better choice of source for comprising words that would better restrict the desired application. However, the results found was too little, just 41. That is the reason why it was decided to evaluate item 7, as it considers a wider range of papers, total of 82.

By analyzing the 82 papers from item 7 (Table 5), it was found that more than half it was related to the mineral industry, in accordance with the supposition made previously base on the journal of origin that most of flotation studies are applied in the mineral processing. It was got only 32 papers focusing on the application of oil removal from water. Due to the proximity of the process and limited availability, any paper investigating oily wastewater treatment was considered in this study, regardless if the application was related to the O&G industry.

This total amount of 32 applicable papers found was considered insufficient for a proper Technological Prospection. Therefore, it was decided to include more papers to the study. Hence, a second research was considered using Scopus database. The Table 7 below shows the results from Scopus website on 10-Jul-2017. The same 10 arranges of keywords (10 items) used in Science Direct were set in Scopus for comparison matters. An extra item (item 11) was also added and will be discussed. Table 8 shows both results – from Science Direct and Scopus.

Table 7: Search results from Scopus on 10-Jul-2017.

Item name	Keyword 1	Location of keyword 1	(AND)Keyword 2	Location keyword 2	Results
Item 1 - flot. @Abst (6430)	flotation	Abstract, Title, keywords	-	-	6430
Item 2 - flot. @Title (2841)	flotation	Title	-	-	2841
Item 3 - @Abst & oil (206)	flotation	Abstract, Title, keywords	oil	Abstract, Title, keywords	206
Item 4 - @Abst& oil water (82)	flotation	Abstract, Title, keywords	oil water	Abstract, Title, keywords	82
Item 5 - @Abst & "oil* water" (17)	flotation	Abstract, Title, keywords	"oil* water"	Abstract, Title, keywords	17
Item 6 - @Abst & "produced water" (16)	flotation	Abstract, Title, keywords	"produced water"	Abstract, Title, keywords	16
Item 7 -@Tit & oil (78)	flotation	Title	oil	Abstract, Title, keywords	78
Item 8 -@Tit & "oil* water" (4)	flotation	Title	"oil* water"	Abstract, Title, keywords	4
Item 9 - @Tit & oil water (22)	flotation	Title	oil water	Abstract, Title, keywords	22
Item 10 - @Tit & "produced water" (9)	flotation	Title	"produced water"	Abstract, Title, keywords	9
Item 11 - @Tit &*oil**water*(135)	flotation	Title	*oil* AND *water*	Abstract, Title, keywords	135

Table 8: Comparison from Science Direct (27-May-2017) and Scopus (10-Jul-2017).

Item nº	Item name	Science Direct	Scopus
Item 1	flot. @Abst	2316	6430
Item 2	flot. @Title	1140	2841
Item 3	@Abst & oil	159	206
Item 4	@Abst & oil water	75	82
Item 5	@Abst & "oil* water"	13	17
Item 6	@Abst & "produced water"	11	16
Item 7	@Tit & oil	82	78
Item 8	@Tit & "oil* water"	9	4
Item 9	@Tit & oil water	41	22
Item 10	@Tit & "produced water"	7	9
Item 11	@Tit &*oil* *water*	*NA*	135

Considering the area of this work, it was noticed that for more general search like the first items, Scopus gave more results than Science direct. On the other hand, for the more restricted researches, as when a second keyword was used, lower quantity of papers was obtained. This was the case of item 7, which was the one selected for evaluation in Science Direct. Hence, it was decided to include an extra logic - item 11 (highlighted with red rectangle) that was doable in Scopus but not in Science Direct. This logic used <*oil* AND *water*>, which considers words derivated from “oil” and “water” - including item 7 that considers only <oil>. By this way, not only more results are obtained but also they could increase the chances of getting more appropriated papers as it considers both keywords.

From the 135 papers listed on Item 11 in Scopus, it was removed the ones already considered on Science Direct list and took off the ones in which the application is not as per this study. In the end it was remaining 36 papers. Summing the 32 papers picked from Science Direct with the 36 from Scopus, it was obtained a final list of 68 papers.

These 68 papers were evaluated and categorized as per the Macro, Meso and Micro classifications previously described. The results and discussion of each are present in the next topics.

4.1. Macro analysis

As posted on item 3.1, the macro analysis comprises the evaluation of the papers with regards the time series (from 2010 to July 2017), countries and affiliation type (university, institution, and company). A greater evaluation can be done with some aspects by analyzing more specifics data when convenient. The results and discussions are presented below.

4.1.1. Time series

The Figure 34 shows a chart with the papers published per year. The year with more publications in the oily water separation study was 2015 with the total of 15 publications. The year with fewer papers in this area was 2011 with only four. It shall bear in mind that for 2017, the research considers only the first months of the year, when the search of this work was done.

Differently from the time series from the papers comprising <flotation> in the title and/or at abstract that showed a progressive growth (given on Figure 33), the set of papers filtered for the oil water treatment presented oscillation of publication through the year, not being possible to determine a trend. A wider range of years would be necessary to verify if there was an overall growth despite fluctuations.

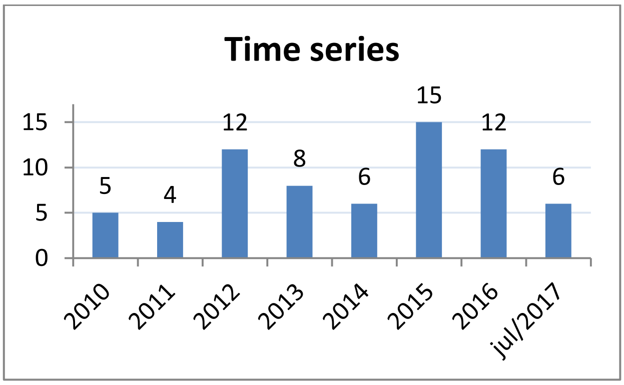


Figure 34: Papers publication per year.

4.1.2. Country

There were 19 different countries among the 68 papers. Some of the papers had affiliations in more than one country. The distribution is presented on Figure 35. As can be observed, China is far on top of the list with more contribution is this area with the 25 papers, followed by Brazil with eight publications. Canada and USA also appear on the top of this list with seven and five papers respectively.

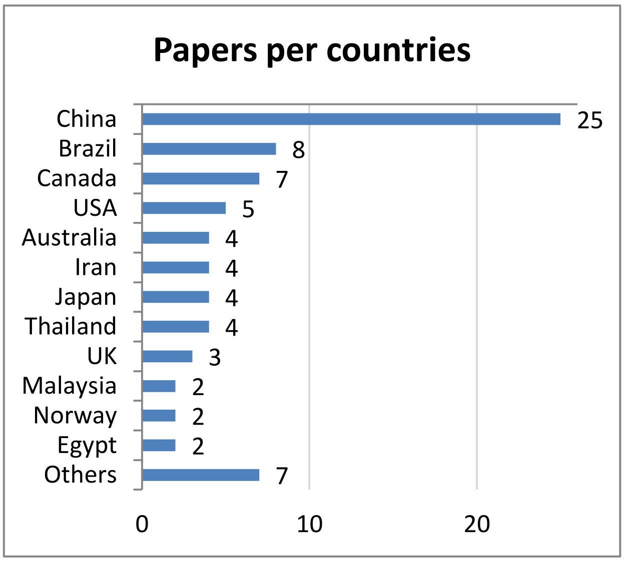


Figure 35: Papers per country

From the 25 Chinese publications, 12 were from General area of application, 11 were from oil and gas industry and the others 2 were one from textile and other from restaurant waste use. Within the 11 Chinese papers from the O&G industry, 5 were specifically from polymer flooding, 5 were from produced water treatment and one from refinery application. With regards the 8 papers in Brazil, 5 were from the O&G industry – all from produced water application, 2 were considered General and 1 is from bioprocess application.

The profile of the results from the top 5 countries in this list are quite similar with the results from the number of flotation columns installed per country reported by Harbort, *et al.* (2017), presented on item 2.3. Therefore, one of the possible reasons for having these countries standing out the researches in the oily water treatment with flotation process may be linked with mineral industry. With the significant production growth of the oil and gas industry in the last years (see Figure 21), research centers that have initially invested efforts in flotation studies applied to the mineral processing, may have benefited from the existing infrastructure and knowledge to include studies applied to the oil and gas industry, as there is a close relation between the processes. Rawlings (2009) remark indorse this hypothesis: "*Treatment of oil well fluids requires the same approach methodology as traditional mineral processing, and uses much of the same unit processes. Approaching the treatment of crude oil as oilfield mineral processing allows technology transfer with the goal of finding optimum solutions for both industries based on two viewpoints*". An observation on item 4.1.3.1, that will be seen ahead, also corroborate with this proposition.

4.1.3. Affiliation type

The information of affiliation is very useful for verifying the main players from the researches. The Figure 36 shows the distribution of the publications according to the type of affiliation, in this case: university and/or institution and/or company.

Universities contribute to 97% of all publications with 66 papers, in which 38 derive only from type of affiliation, followed by the partnership of institutions with the contribution of 14 papers, followed by partnership with companies, with 12 publications.

Institution individually comes in the second place, with 18 papers, which is 26% of the total. Company is the last in the list, being the affiliation with less contribution to papers in this study, with 15 papers, that represents 22% of the total. There was no paper linked solely with company.

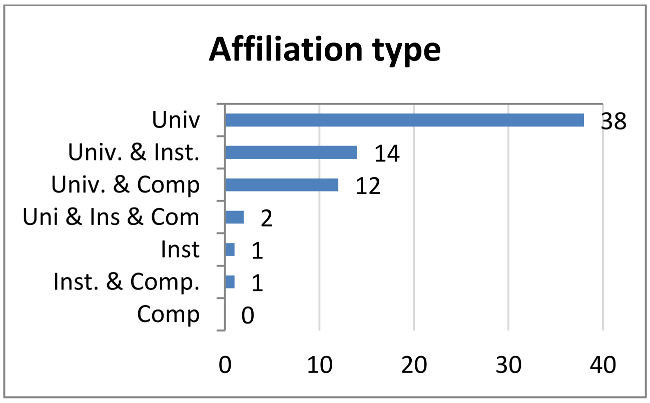


Figure 36: Affiliation type distribution.

4.1.3.1. Main players on Papers

The set of 68 papers comprised 81 different affiliations, sorted by university, institution, and company. The Figure 37 shows the main ones. ‘China University of Mining & Technology ’is the player with more papers with eight publications. All of them related to the study of a specific equipment, as will be seen ahead.

An also Chinese institution and company are tied for second place in the rank of players, respectively ‘Beijing Institute of Petrochemical Technology’ and ‘Sinopec’, with 5 papers each. Brazil is part of the rank with ‘Universidade Federal do Rio Grande do Sul’ (UFRGS) and ‘Universidade Federal do Rio Grande do Norte’ (UFRN) with three papers each.

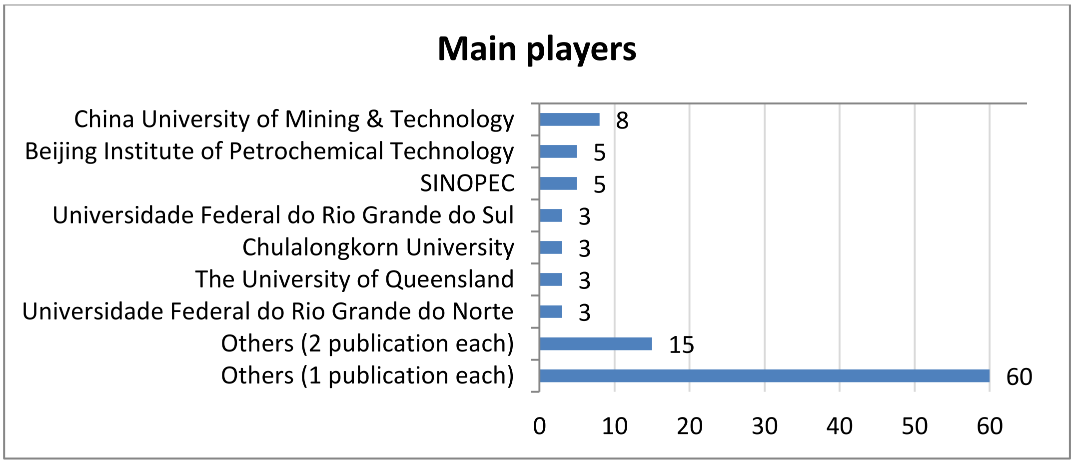


Figure 37: Main affiliations regarding the analyzed papers.

From the 11 companies, only two of them had more than one publication: MI-Swaco with two and Sinopec with five. Considering that companies had relatively less contribution of papers compared to other affiliations, it is an interesting fact to find Sinopec as a second in this rank. It shows a potential engagement of this player with research and development area. The works had contribution from different branches of the company, and the papers were mostly applied to general area with equipment tests.

All the 8 papers from the ‘China University of Mining and Technology’ was related to a study of a specific type of equipment: cyclonic-static micro bubble flotation column (FCSMC).

For the UFRGS papers, they were all from the *Laboratório de Tecnologia Mineral e Ambiental* (Laboratory of mineral and environmental technology), from the *Departamento* *de Engenharia de Minas* (Department of mining engineering). The center name linked to the mineral area also corroborate with the hypothesis posted in the country analysis that correlates studies of flotation applied to oily water to mineral flotation.

It is interesting to highlight that professor Jorge Rubio was one of the authors from all these UFRGS papers and is a reference in Brazil for flotation process. His work "*Overview of flotation as a wastewater treatment technique*" (Rubio, et al., 2002) was the paper with more downloads in the periodic in 2002 (Matiolo, et al., 2003), and has been cited 385 times (according to Science Direct on 16/08/2017).

4.2. Meso analysis

In this stage, as mention on item 3.1, taxonomies are set for Meso based on the contents of the documents. Each of them are, then, studied. A more detailed evaluation can be done with some of the taxonomies by analyzing more specifics data, which correspond to the Micro analysis. The results and discussions are presented below.

4.2.1. Taxonomy for the papers

The papers were read and analyzed. The main tendencies were identified to establish the taxonomy, in order to organize the investigation of the information.

It was noticed that all papers were related to three types of researches: experimental, computational and/or as a review. With regards the sector of application related to the oily water treatment, although most of the studies are associated with the oil and gas industry, other areas of application also motivated the works. So, it was decided to consider it as one taxonomy.

It was expected to find clear information about the type of flotation and type of equipment within most of the papers due to their relevance to the process, however, not always it was evidenced. Both were considered interested to evaluate. The main area of study varied among the references and were also considered for analysis to access the trend of the researches.

The five taxonomies are summarized below:

- Research type: if the study was made by means of experiment, simulation/computational, review or a combination of them.
- Sector of application: the area of application of the studied process. For instance, Oil & Gas, Mechanic, Bioprocess, Food, etc. For the cases there was no specific industry it was classified as "general".
- Flotation type: the type of the flotation process being studied, when specified. For example, dissolved gas flotation, Induced gas flotation and electro-flotation. For cases where flotation process was studied for any application, and/or as an overall review, it was considered as "general".
- Apparatus type: the type of cell used in the research. For instance, electroflotation cell, cyclonic type, mechanical induced, etc.
- Main area of study: the topic being investigated, as operating parameters, chemicals study, monitoring solutions (instrument, control, etc.), equipment test and design and prediction model.

4.2.2. Research type

The Figure 38 shows the charts related to the research type. Most papers were based in experimental studies, with 57 of them considering it. In second place comes review type with 8 papers. In the last position is simulation type of study with 6 papers, in which half of it also considered experimental tests.

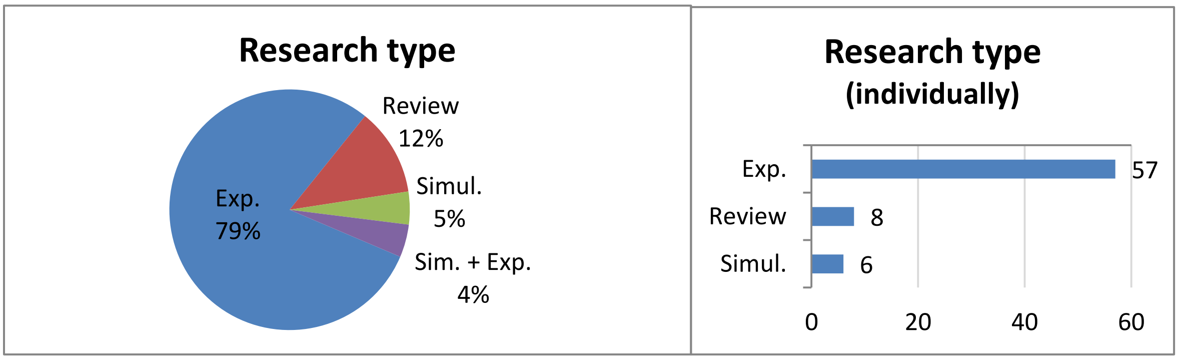


Figure 38: Research type with the main set of 68 papers. Respectively: percentage of publications and individual quantity of each type.

One example of simulation-based paper is the "Numerical studies on dynamic characteristics of oil-water separation in loop flotation column" that performed CFD simulation to research the dynamic separation characteristics of oil droplets and oil-water separation efficiency under different circulation flow rates. This paper also performed experimental test to validate the numerical simulation, representing a case of experimental paper as well. An example of paper performing a review is the "Alternative flotation techniques for wastewater treatment: Focus on electroflotation" that revises the application of flotation in the treatment of waste from different industries, especially the application of electroflotation.

It is comprehensive that most of the studies are based on the experimental test considering it is a process governed by many variables and has a close dependence to the characteristic of the fluid. This creates a demand for testing each new scenario/application.

Micro analysis

From the experimental studies, 6 mentioned that the test was performed under pilot scale and 4 under field plant/full scale application. The players related to pilot scale tests are originated from Canada, USA, Brazil, China and Iran. Example of affiliations are: 'Universidade Federal do Rio Grande do Sul', 'National Iranian Oil Company' and 'Centre for Management of Technology and Innovation', that represents respectively an university, company and institution. With regards the full-scale research, three were Chinese and one was a partnership of Iran and Canada. The players are 'China University of Mining and Technology', 'Razi Univesitity', 'University of Guelph', 'Beijing Institute of Petrochemical Technology', 'Chinese National Engineering Research Center of Coal Preparation and Purification' and 'Sinopec'.

For all the simulation based papers the study was made on the Computational Fluid Dynamics, being the hydrodynamic the main investigated area. A player with highlight in the simulation research is the 'Beijing Institute of Petrochemical Technology' contributing with 3 documents out of the total 6 papers. The demand of studies for better understanding this subject was underlined by Xinga, *et al*. (2017) in the paper of this year called *Recent experimental advances for understanding bubble-particle attachment in flotation*: "Various hydrodynamic conditions can be found in a flotation cells and it plays an important role in bubble-particle interaction. The synergistic effect between surface force and hydrodynamic force requires further studies".

4.2.3. Sector of application

As mentioned before, while picking out the papers it was selected the ones applicable to oily water treatment. Some of these papers were specifically aiming the oil and gas industry application. Others made the research targeting mechanical industry, like the studies with motor oil and cutting oil. There were papers handling wastewater contaminated with vegetal oils, nuclear waste, etc. When the papers mentioned generically oily water it was considered as "general". This classification was also considered for the review type papers when it was the case of general application. The results can be found on Figure 39.

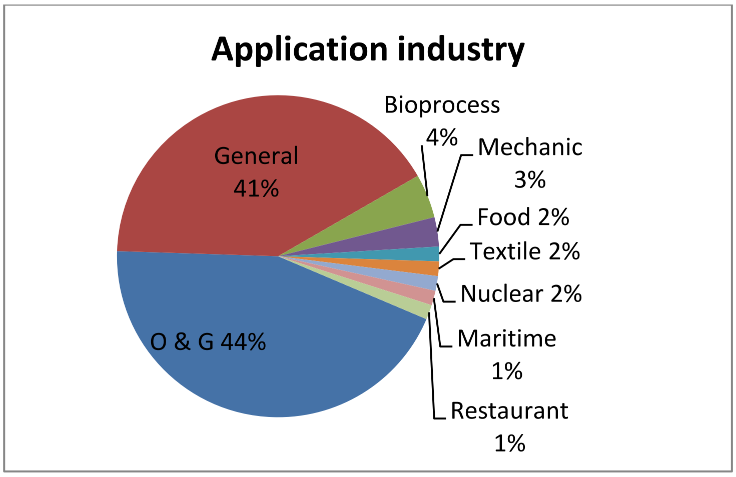


Figure 39: Sector of application within the main set of 68 papers

As can be seen, the specific sector with, by far, more studies were the oil and gas industry, with 30 papers, which represents 43% of the total. Many papers were classified as general application, with 28 documents. Several other sectors had small percentages of contribution, like the bioprocess, mechanic, food, textile, nuclear, maritime and restaurant.

Two cases from the O&G industry papers are the "Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles" and the "Cyclone-air flotation technology and its application in oil removal pre-treatment for electric desalting wastewater", with respectively application in the oil primary processing and oil refining.

Example of a General application case is the paper "Removal of fine oil droplets from oil-in-water mixtures by dissolved air flotation" that tested a "generic" emulsion. A paper related to the Bioprocess is the "Treatment of biodiesel wastewater by electrocoagulation/flotation process: Investigation of operational parameters" that as per the tittle investigated waste from biodiesel production by applying electrical field. An example of the Textile sector application is the "Effect of micro-bubbles on coagulation flotation process of dyeing wastewater" that compared essentially two bubble sizes (referred as micro and conventional) as pretreatment of dyeing wastewater. From the Restaurant waste application there is the "Separation of pollutants from oil-containing restaurant wastewater by novel microbubble air flotation and traditional dissolved air flotation" that compared two flotation processes in the restaurant oily waste treatment. An example from Mechanical application is the "Cutting oil removal by continuous froth flotation with packing media under low interfacial tension condition" that analyzed effects of operational parameter under specific scenario. From the Nuclear area one example is the "Dissolved air flotation for treating wastewater of the nuclear industry: Preliminary results" that tested the DAF with chemicals to determine operational variables.

Micro analysis

The O&G industry comprises an extensive range of processes, which is one of the reasons for having numerous publications in this field, together with its importance to the economy compared to the other areas. The distribution of the different applications found within the oil and gas industry is presented on Figure 40.

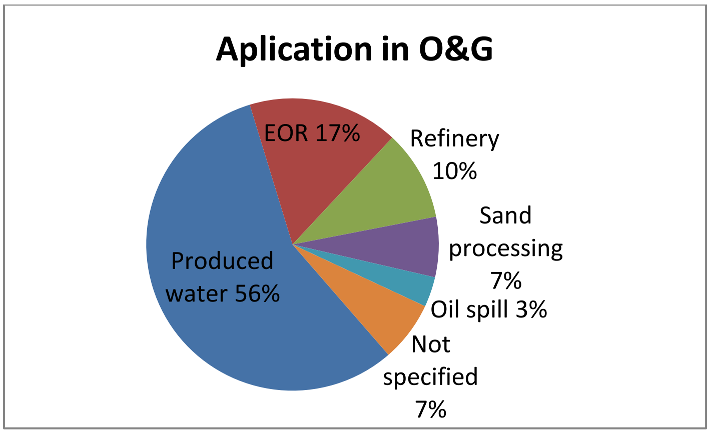


Figure 40: Application inside the oil and gas industry within the 29 papers from this sector

More than half of the papers were directing the studies specifically to the produced water treatment. The second most studied area inside O&G was the wastewater from increase oil recovery (EOR) activities, which results in contaminating the water with residues from polymer flooding. Other applications were: refinery waste, sand processing residues (characterized by bitumen presence) and oil spill.

The main players from the oil and gas industry were 'China University of Mining & Technology' that published four papers on this area and 'Universidade Federal do Rio Grande do Norte' that contributed with three papers. There were other eight affiliations that had two publications on the O&G industry and 29 others contributing with one paper each.

All five studies from EOR application found on the list of this study had a contribution from a Chinese affiliation. The main player was 'China University of Mining & Technology' with three publications and 'China University of Mining and Technology' and 'Northeast Petroleum University' with two each.

4.2.4. Main area of study

Evaluate the content of the papers is important in order to identify the areas that currently have being receiving more investigation on this process. The set of 68 scientific papers included tests related to equipment as the "Loop flotation for oil-containing water treatment" that make use of an equipment enclosing loop feature; and the "Performance analysis of a novel compact flotation unit" that, as per the title, tests a CFU. Chemicals were also researched as in the "Effect of biosurfactant addition in a pilot scale dissolved air flotation system" that states environmental gains by using biodegradable additive; and the "Performance enhancement of dissolved air flotation column in removing low concentrations of heavy fuel oil by adding powdered activated carbon" that studied the effect of adding walnut-shell based powdered activated carbon on oil removal. Flotation process related to other processes were also among the scope as in the "Oil removal from produced water by conjugation of flotation and photo-Fenton processes" and "Dissolved air flotation and centrifugation as methods for oil recovery from ruptured microalgal cells" that studies flotation combined with photo-Fenton and compared to centrifugation, respectively. Models are also presented by some studies as in "Modeling an industrial dissolved air flotation tank used for separating oil from wastewater". The Table 9 presents the main area of study from the papers.

Table 9: Main areas of study

Rank	Area of study	Papers quantity	Percentage
1	Related to equipment	38	56%
2	Chemical(s)	23	35%
3	Relation with other equipment/process	15	22%
4	Model	14	21%
5	General	7	10%
6	Monitoring/Control	3	4%
7	Other	2	3%

More than half of the studies made equipment tests in order to investigate operational parameters and/or analyze the performance in a specific application. There were design improvement, optimization, modeling, and other goals. This result is understandable considering that flotation process has no universal prediction model, i.e., every new scenario requires its own examination. Wang *et al.* (2010) statement in DGF section corroborate with this finding: "It is recommended to test the actual wastewater to be treated on a pilot-scale before embarking on the design of a full-scale DAF unit". In addition, there is a wide range of equipment types, in different stages of developments, that demand research for improvements (in the design and operational) and/or for broad its application.

Chemicals/additives, such as coagulants and flocculants, is the second most studied area with 21% of the total. From the 23 papers comprising a chemical analysis, 10 were focusing this study in the first place. This result shows the considerable importance of it on the flotation process.

There were 15 papers (22%) investigating the relation between processes or equipment for a comparison or a combination among them. The comparison study can be considered a form of equipment research that uses similar tools as reference. The combination may be linked to the usage of one of them as an auxiliary process and/or as part of a wider approach over different stages of wastewater treatment. This tactic is useful to evaluate interfaces and the synergistic effect of multiple process. It shall be clarified that coagulation and flocculation were not considered a combination type of process, although some authors did so. For this study, both were approached as part of the chemicals usage in the flotation process, which as seen before, is also a category within this taxonomy. This assumption was based on the fact that many experiments used coagulants and flocculants within their flotation tests.

Bellow in the rank it is fond: 21% of the papers that provided prediction models, such as kinetic models and mathematical models; 10% were considered "general" for been a general overview and/or comprising an extensive range of areas; 3% studied monitoring tools, such as control and instrumentation; and two papers were not considered on the previous classifications for studying particular areas: one studied multiphase pump applied for flotation process and the other a specific process variable – salinity.

Micro analysis

From the papers related to equipment, 76% tested operational parameters and 18% focused on design improvement.

Among these main areas of study, 31 papers (46%) studied operational parameters, i.e., the influence of different variables on the performance of the process. The gas rate was the most studied parameter, followed by the waste characteristics (flow rate, oil concentration and composition). Both are very important parameter on flotation process as observed on the literature review. Pressure, residence time, salinity and pH were also considerably studied variables among the papers.

The relation between flotation with two or more processes or equipment types are the following: 9 papers performed combination and 8 did comparison. The most compared/combined studies were between two flotation processes/equipment type with a total of 5 papers. Comprising 2 papers each there were: Filtration, Photo-Fenton, Oxidation and Adsorption processes. There was also one paper comparing centrifugation with flotation. All of these processes are applied to the waste water treatment and may give benefits for being associated with flotation.

4.2.5. Flotation Process type

The flotation process type not always were clearly mentioned within the documents. For some papers it was possible to infer based on supplementary information, others remained unknown. For the papers with a review or approaching several types, it was considered as “general”. The results are shown on Table 10.

Table 10: Flotation process type

Flotation process type	Papers quantity	Percentage
Induced	30	44%
Dissolved	24	35%
Electro	5	7%
General	6	9%
Unknown	7	10%

The two most researched flotation type in the studies were the induced and dissolved gas flotation systems. This result is aligned with the literature report of both processes being the two most commonly used flotation technologies (Saththasivam, et al., 2016)(Rawlins, 2009)(Wang, et al., 2010).

Comprising 44% of the papers and 30 documents, the induced gas flotation is in the top of the list. This may be linked with the fact that many studies aimed equipment tests and developments. As seen before (item 2.1.1.2), in this process there are different ways of bubble generation and consequently it comprises a wide range of equipment.

In the second position is the dissolved gas flotation with 24 papers, 35% of total. As reviewed previously (item 2.1.1.1), this process generates small bubbles and they may nucleate from the oil droplets which makes this flotation type handy for wastewater containing emulsified oil, which is difficult to separate.

There are fewer studies (7%) considering the electro-flotation compared to the other two technologies. This is equitable considering that oily water treatment is not traditionally the field of application of this flotation type due to hydraulic loadings and cost barriers (seen on item 2.1.1.3). Yet, it is interesting to see that there are investigations going on in this area. Depending of future developments, it could lead to an expansion of this usage.

Micro analysis

Papers studying electroflotation in general investigated equipment design and operating parameters for different scenarios such as O&G (sand tailing and primary processing), Maritime and Bioprocess.

Figure 41 presents the main area of study among the induced gas flotation papers. Equipment investigation was the main area of study with 20 papers. The second most studied area, with 10 papers, was the chemical(s) and the third, with 3 papers, was the relation with flotation and other process.

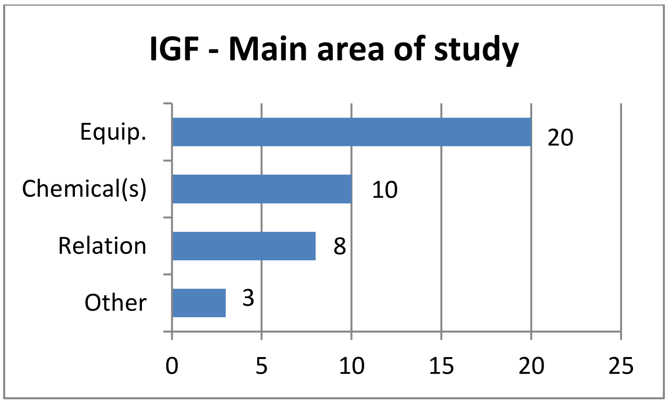


Figure 41: Main area of study within induced gas flotation

Figure 42 presents the main area of application and apparatus type within the IGF. Almost half (47%) of the induced flotation studies focused the oil and gas industry. There were 33% documents with a general approach. Other areas were mechanical, bioprocess, textile, restaurant waste and food. With regards the apparatus type, 26% was related to the research of the FCSMC, 26% was columns, 9% was loop flotation and 39% were related to other types, as mechanically induced, CFU, venturi, etc. This variety of apparatus supports the presumption for having the majority of papers investigating IGF due to the diversity of apparatus type, mentioned before.

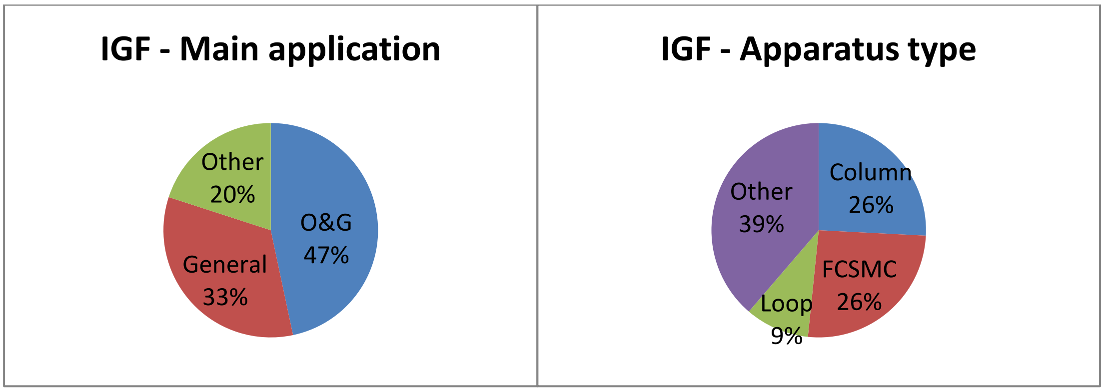


Figure 42: Respectively, main areas of application and equipment type from the 30 patents of induced gas flotation type

Figure 43 presents the main area of study among the dissolved gas flotation papers. Chemical investigation was the most studied area with 11 papers. The second and third, with nine and six papers respectively are the study relating flotation with other process and the studies related to equipment.

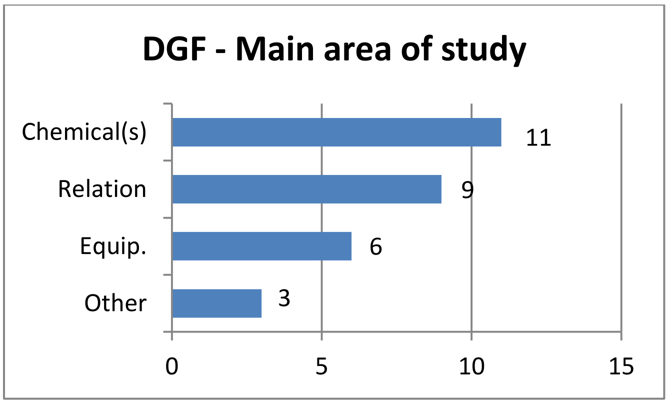


Figure 43: Main area of study within dissolved gas flotation

Figure 44 presents the main area of application and apparatus type within the DGF. Half of the dissolved flotation studies were focusing the oil and gas industry. There were 33% documents with a general approach. Other areas were bioprocess, textile, restaurant waste and nuclear. With regards the apparatus type, 33% was classified as “unknown” due to no directly nomenclature for the apparatus, 21% was from column type, 21% tanks, 17% jar test and 8% other types. As will be seen further, many of these apparatus types may be related to experimental device. It is notable the smaller diversity of equipment of DGF compared to IGF, analyzed before.

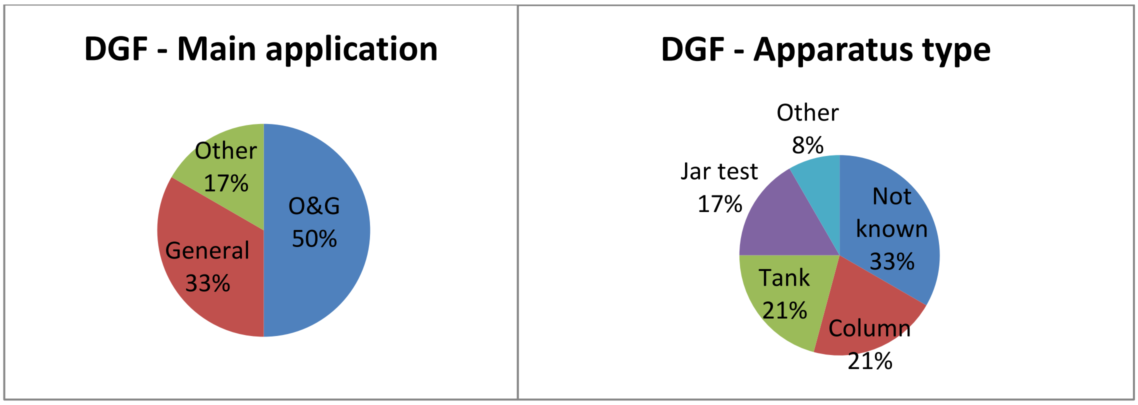


Figure 44: Respectively main areas of application and equipment type from the 24 patents of dissolved gas flotation type

4.2.6. Apparatus type

Like the flotation type, the apparatus type were not always explicit in the paper. Type were listed mostly according to the given name, and few were possible to infer based on other information, like the experimental description. Some works studied specific models as the compact flotation unit and Jameson cell. Other papers specified key features of their apparatus like cyclonic flow pattern, venturi type of introducing bubbles, etc. There were also generic description of columns and tanks where no special characteristic was mentioned. And, as in most of the taxonomies, there were also general studies and cases where more than one device was used. The apparatus/device type list can be seen on Table 11.

Table 11: Apparatus type

Apparatus type	Papers quantity	Percentage from all publications
Column	12	18%
Cyclonic static micro-bubble flotation column (FCSMC)	8	12%
Tank	7	10%
Compact flotation unit (CFU)	6	9%
General	6	9%
Loop flotation	5	7%
Electro-flotation Cell	5	7%
Jar test	4	6%
Cyclonic	2	3%
Mechanically Induced	2	3%
Venturi	1	1%
Convention and modified jet (Jameson) cell (CJC and MJC)	1	1%
Unknown	11	16%

A considerable variety of apparatus and devices were used within the research studies. General designation of columns and tanks were highly reported representing respectively, 18% and 7% of the 68 papers.

The two-specific models most researched were the FCSMC and the CFU. They are relatively new types and under studies for improvement. Both are lined up with the latest generation trend of offshore flotation cells that are primarily hydraulic IGF or DGF (Rawlins, 2009). An interesting fact is that both cells involve the cyclonic flow field that make use of centrifugal forces for improving the separation, which may be an indication of a trend in the usage of this flow characteristic on the improvement of equipment performance. Both also have small footprint which is beneficial for constrained areas.

Loop flotation, which considers internal flow circulation on the column, was part of 7% of the papers. No specific apparatus model was inferred from the studies. This feature was considered a generic device with a loop flow characteristic.

The electro-flotation cell, that is the equipment associated with electro-flotation process, was part of 7%.

Jar test is a set of batch beakers with a paddle mixer for each one. It is a test apparatus commonly applied in water related experiments. This machinery was utilized in 4 works. It is a comprehensible apparition as it is a useful system for comparative investigations, which is the case of chemical type and/or dosage.

There were 11 papers with no specific name for the apparatus, referred as “unknown”. Together with the jar test, some columns and tanks are standard experimental apparatus for testing the process, as mention of item 2.5 and supported by the Handbook of Environmental Engineering (Wang, et al., 2010) which illustrates jar test, bench cells and laboratory scale items (columns, tanks, pipes, pumps, instruments, etc.) assembled according to the desired study.

Other types of machinery and features were also observed, though in lower number, in the research works as cyclonic, mechanically induced, venturi and Jameson cells. The reduced amount of papers is possible linked to fact that they are comparatively older technologies which means a lot had already being developed to them, since they started to be researched at an earlier time.

Micro analysis

The FCSMC experiences mostly aimed operating parameters analysis, mainly: circulating pressure, aeration rate and chemical (frother) composition. A large amount of them also provided prediction models. This is a considerable new type of apparatus, consequently, it still demands researches from its creator - ‘China University of Mining and Technology’, which is author from all the 8 papers from FCSMC, as mentioned before.

The CFU was the apparatus with more variety of research. There were design/geometry study, instrumentation application, field test, hydrodynamic evaluation and performance analysis. The main players related to this model were the ‘Beijing Institute of Petrochemical Technology’ with 3 papers and the partnership of ‘M-I Swaco AS’ and ‘Telemark University College’ with 2 papers.

For the Jar test, all of the experiments utilized dissolved gas flotation process type, and half of them were applied for the study of chemical(s) and the other half to the comparison /combination between two processes.

The electro-flotation cells were evidently all related to electro-flotation type. They tested their application in specific cases and investigated optimal equipment design parameter such as electrode distance and most favorable current value. Other operational parameters also studied within this apparatus were pH and residence time. There were no in-common players neither countries among the papers. All of them had a single affiliation – all university type, i.e., there were no partnership.

4.3. Conclusion from papers

A set of 68 papers taken from Science Direct and Scopus databases were evaluated. The analysis showed that dissolved and induced gas flotation technology were the most common process type investigated within flotation applied to the treatment of oily wastewater, with the IGF being slightly bigger than DGF. There were also researches of electroflotation process but with less expressiveness compared to the rest.

More than half of the studies focused on operational parameters and performance of equipment in a specific application. There were design improvement, optimization, modeling, and other goals. Chemical additives also were noticeably studied as coadjutants in this process, as well as prediction model developments for specific applications.

Among process variable, the gas rate was the most studied, followed by the waste characteristics (flow rate, oil concentration and composition) – in accordance to the reports of literature. Pressure, residence time, salinity and pH were also considerably studied variables among the papers. The two first are important variables in the equipment operational performance, and the last two crucial solution properties. These results, besides pointing out relevant parameters in the process, show the multivariable face of gas flotation.

Universities contribute to 97% of all publications, and 84% of the researches were based on experimental tests. The simulation studies were all from Computational Fluid Dynamics (CFD), most of them investigating the process hydrodynamic.

The three top players were Chinese and the one with more contribution was the 'China University of Mining & Technology'. China and Brazil were the countries with more publications in this field on this study. The Oil and gas industry was the main sector of application of the researches in which most of the purposes were associated to the produced water treatment.

The two specific apparatus models with more incidence of research were the cyclonic state micro-bubble flotation column (FCSMC) and the compact flotation unit (CFU). The fact that both comprises rotation flow is a high indication of a trend in the application of circular field to take the advantage of the centrifugal force on the process separation. Studies specifically on the process hydrodynamic corroborates the interest in flow pattern gains. Moreover, both models are vertical column, which minimize floor area, and have no moving parts.

5. RESULTS FROM THE PATENTS TECHNOLOGICAL PROSPECTION

The general results from different searches in USPTO and INPI is shown on Table 12. It gives an overview of the documents quantity related to the flotation considering a diverse combination of keywords and its location. Similar specifications from the papers research were applied for patents. It was chosen to specify the same date range from the papers (Scopus), i.e., from 1st January of 2010 till 10th July of 2017.As INPI is based on the Portuguese idiom, the corresponded word is presented in italic.

Table 12: Search results from USPTO and INPI.

Item name	Keyword 1	Location keyword 1	(AND)Keyword 2	Location keyword 2	USPTO	INPI	Total
Item 1 - flot. @Abst	flotation/ *flotação*	Abstract	-	-	531	92	623
Item 2 - flot. @Title	flotation/ *flotação*	Title	-	-	276	60	306
Item 3 - @Abst& oil	flotation/ *flotação*	Abstract	oil/ *óleo*	Abstract	29	12	41
Item 4 - @Abst& oil water	flotation/ *flotação*	Abstract	oil water/ *óleo água*	Abstract	17	6	23
Item 5 - @Abst& "oil* water"	flotation/ *flotação*	Abstract	"oil* water"/ *oleosa*	Abstract	5	2	7
Item 6 - @Abst& "produced water"	flotation/ *flotação*	Abstract	"produced water"/ *"água produzida"*	Abstract	4	0	4
Item 7 -@Tit & oil	flotation/ *flotação*	Title	oil/ *óleo*	Abstract	10	7	17
Item 8 -@Tit & "oil* water"	flotation/ *flotação*	Title	"oil* water"/ *oleosa*	Abstract	2	0	2
Item 9 - @Tit & oil water	flotation/ *flotação*	Title	oil water/ *óleo água*	Abstract	6	3	9
Item 10 - @Tit & "produced water"	flotation/ *flotação*	Title	"produced water"/ *"água produzida"*	Abstract	1	0	1

It was found 276 patents containing the word <flotation> in the title in the USPTO and 60 on INPI. Restricting the specification to also consider a second keyword <oil> in the abstract, there were only 29 patents on USPTO and 12 on INPI. As few results were obtained by restricting the search with a second keyword, it was decided to choose the item2, which has 306 patents, as list of evaluation – highlighted in red on the table.

Differently from the papers research, a considerable number of patents were not linked to flotation process. It was the case of floatable devices such as life jackets, floating seats, recreational toys, boats, etc. For this reason, in USPTO the cut tool <ANDNOT> was applied to clean up the list with undesired type of recurrent items.

As mention before, some patents from INPI base did not have available all information, as abstract or a detailed description of the system. Therefore, some patents were excluded and some cases had part of the classifications set as "unknown".

As occurred in the paper analysis, the application was related to mineral processing in many documents. However, in many cases, patents mentioned a possibility of application its invention in further cases, regardless the original motivator, as a way to cover the maximum number of application. Thus, for this study, patents that had very specific applications in other industries were removed and the inventions considered suitable for oil-water separation were selected.

From the original 306 documents, it was obtained a final list of 58 in which 42 were from USPTO and 16 were from INPI. These documents were evaluated and categorized as per the Macro, Meso and Micro classifications similarly to the papers. The results and discussion of each are present in the next topics.

5.1. Macro analysis

As posted on item 3.1, the Macro analysis comprises the evaluation of the patents with regards the time series (from 2010 to July 2017), countries and assignee type (university, institution and company). The results and discussions are presented below.

5.1.1. Time series

The Figure 45 shows a chart with the patents time series. Similar to what has happened in the papers analysis, the quantity of documents varies through the year. The year with more publications in the oily water treatment applicable invention for INPI was 2014 with the total of 9 publications, for USPTO the year with more documents were 2016 with a total of 12 patents. From the total aspects, these both years are the biggest pics, and the years with less patents in this area were 2010 and 2015, not counting the 2017 that consider only part of the year.

A second chart with the historical distribution of patents separated by the most predominant sectors (analyzed further in item 5.2.3) is given on Figure 46. It can be observed that the highest peaks are from a variety of non-predominant sectors on this study.

Considering the oscillation of patents registration within the time series considered for this work, it is not possible to get conclusions concerning growth tendencies.

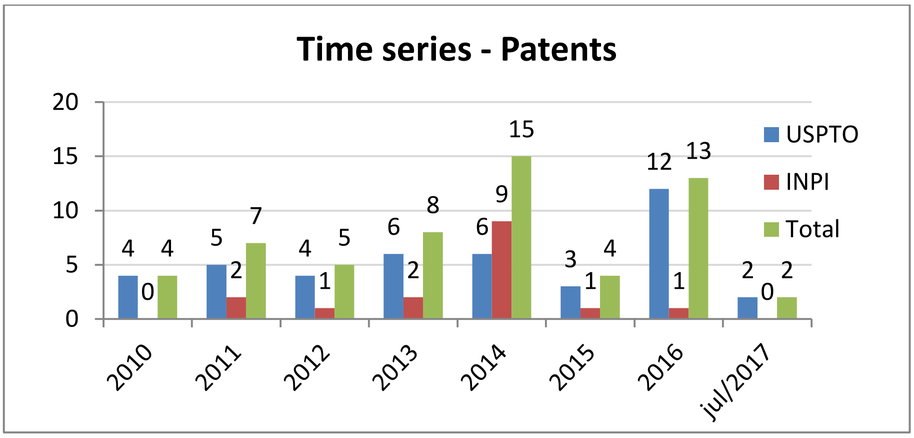


Figure 45: Patents time series

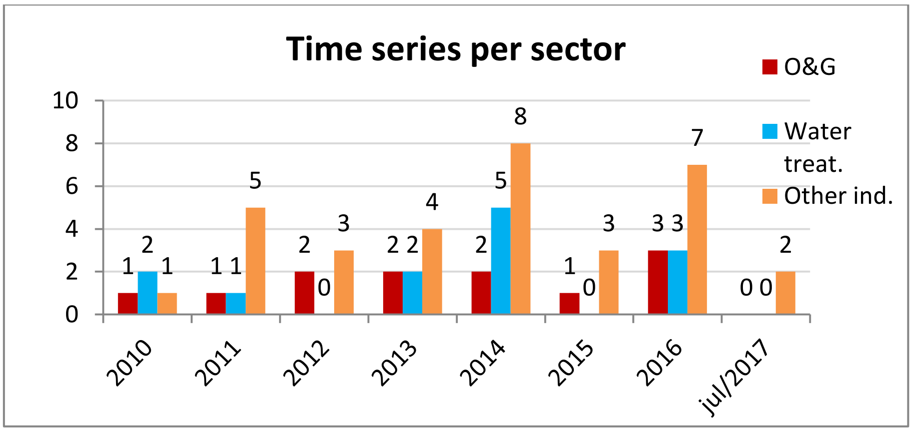


Figure 46: Time series comparing O&G and water treatment patents (both USPTO and INPI bases)

5.1.2. Country

For the classification of the countries, it was considered the country of the assignee in the USPTO and the country of the depositor (<*depositante*>) in INPI, which are fields where the specifications were located. USPTO has additionally the countries of the applicants and invertors. There were cases with inputs of more than one country.

There was a total of 10 different countries within the USPTO list and 6 in INPI. The distributions are presented on Figure 47. As can be noticed, USA is the most publisher from USPTO base and the second most from INPI. By summing up its patents from both bases, there were 24 patents, way more than any other country in the list. For INPI, the country with more contributions was Brazil, which is reasonable considering it is a Brazilian base.

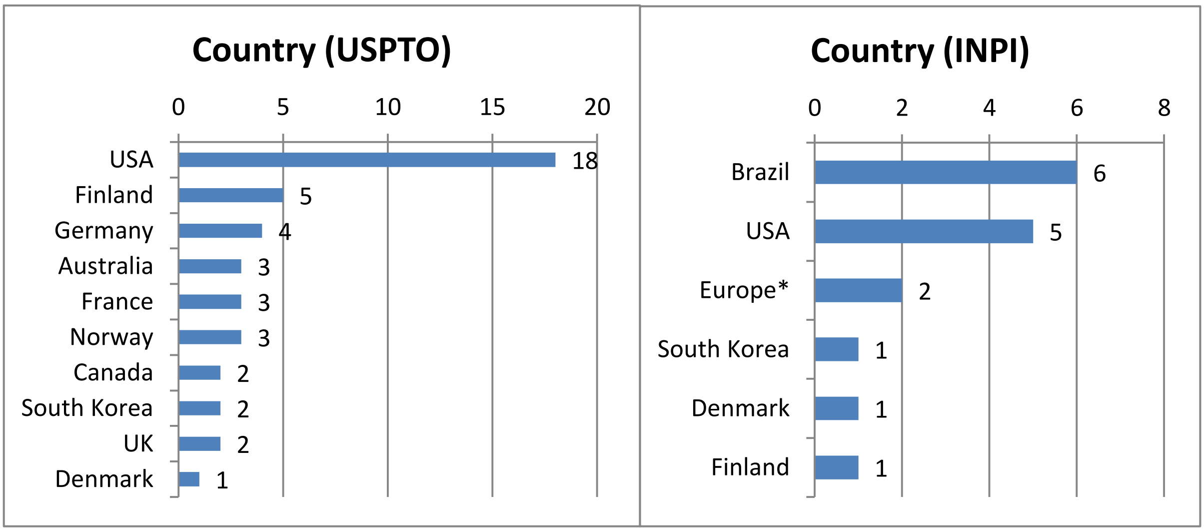


Figure 47: Patents per country.

* "Europe" labeled after the "*Organização Européia de Patentes*" (European Patent Office) as per filled in the country field.

It is curious to observe that China is not in the list from USPTO neither INPI (of this work), while in the papers study it was by far the most contributor. In order to investigate this output, the ESPACENET - which is the European patents base - was quickly researched. Out of the 387 patents with <flotation> on the title and <oil> in the abstract within the same period of this work, 343 were from China, which represents 89% of the total (without filtering the application of invention). It shows that China do patent its inventions. One of the hypothesis could be that the Chinese companies are not focusing on the Americans continents. However, only a deeper analysis of this patent bases together with a market study to come up with a solid explanation for this.

It is interesting to mention the main players from countries in the top of the rank. Table 13 shows the main players from USA. ‘Cameron’, ‘Sionix’ and ‘Ecolab’ had four patents each, with the last one with documents in both bases. The Ecolab patent in the USPTO base is the “Composition and method for improvement in froth flotation” and it seems to be of the same content of one of the INPI´s base. It claims a method that uses a chemical to improve the effectiveness of an emulsifier. INPI does not supply detailed information to confirm this supposition.

Table 13: American main Players

Players	**USPTO**	**INPI**	**Total**
Cameron	4	-	4
Sionix	4	-	4
Ecolab	1	3	4
Virginia Tech Intellectual Properties	2	1	3
Exterran	1	1	2

Finland´s top position in this work is credit from the company ‘Outotec Oyj’- which is from the mineral industry, which was author of 5 documents out of the 6 Finnish patents (considering both bases). The other assignee was ‘Geologian Tutkimuskeskus’ – a company which most of business is also related to mineral industry.

Within the six Brazilian patents, there were five different players. The only one with two documents was from ‘*Centro de Gestão de Tecnologia e Inovação*’, which is a R&D center with four units spread through North, Northeast and Southeast of Brazil. The only Brazilian company is the ‘Alkem Equipamentos Industriais’, a company that provides industrial equipment for water treatment among others. The other three Brazilians assignees are spread between two different universities and one natural person. Regarding the state of origin in Brazil, there were two from São Paulo, two from Pernambuco, one from Ceará and one from Rio Grande do Sul. The main players overall patents are presented on item 5.1.3.1.

5.1.3. Assignee type

The information of assignee type is divided by company, institution (or center), university and no assignee or natural person. This analysis brings relevant information on the players profile. The distribution is shown on Figure 48 bellow.

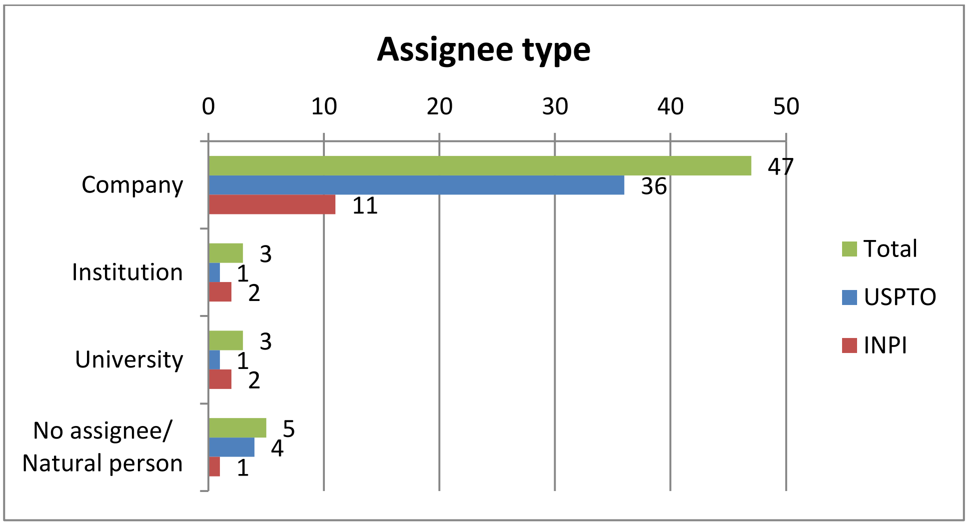


Figure 48: Assignee type distribution.

Differently from the profile of the papers publishers that had a majority of academic origin, the patents have more contribution from the industry. This results are consistent with the characteristic of each area - while researches are more common to be executed in universities, the industries tend to focus their developments in production applicable inventions. Companies were responsible for 81% of the total, by far the biggest assignee type provider. The business area of these companies are analyzed on item 5.2.3.

5.1.3.1. Main players on Patents

The set of 58 documents comprised 28 different assignees. The Figure 49 shows the ones with more patents spread through both bases. 'Outotec Oyj' is the player with more inventions in this work, with five patents. It is a Finish company in the Mineral business. The American companies 'Cameron', 'Sionix' and 'Ecolab' already mentioned before are the second in the rank with four patents each. 'Doosan', 'Exterran', 'Schlumberger', 'Siemens' and 'Virginia Tech Intellectual Properties' come next with three patents each. It is important to mention that some assignee had more than one patent related to the same invention, being extra patents applied to include improvements of further developments. Moreover, there were patents concerning the same (or very similar) invention from equal assignee in both bases.

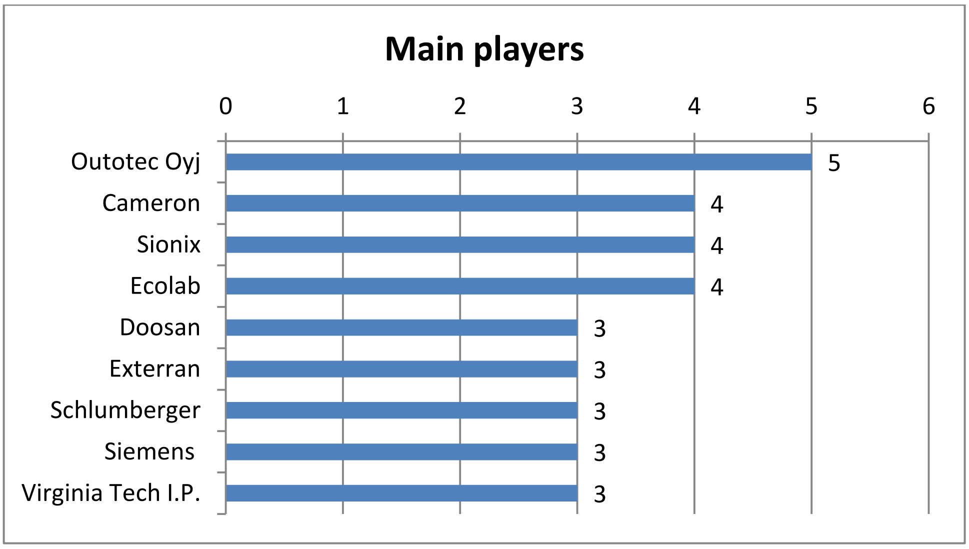


Figure 49: Main assignees/players

The Brazilian company 'Alkem Equipamentos Industriais' has diverse business with water treatment branch. Its patent is related to an equipment for the electroflotation process, as will be seen further.

Table 14 presents the players with more patents in this work and the Brazilian company, comprising the country of origin, the number of patents and the business description and website. Specific analysis of the sector of the players is presented on item 5.2.3, where the businesses are grouped in few sector categories.

Table 14: Summary of the main players. The Brazilian company was also listed.

Player	Country	Patents	Business description and Website
Outotec	Finland	5	Core business is the mineral processing comprising services and metal, energy and water solutions. – https://www.outotec.com/
CAMERON A Schlumberger Company	USA	4	Cameron is a Schlumberger company acting on the O&G industry. Main areas related to flow and pressure control technologies. – https://cameron.slb.com/
SIONIX CORPORATION	USA	4	Water treatment solutions with a patented DAF technology as the heart of their systems. – http://www.sionix.com/
ECOLAB®	USA	4	Water, hygiene and energy technologies and services. – http://www.ecolab.com/
DOOSAN	South Korea	3	Diverse business with water treatment branch. Multiple business comprises power generation, desalination, engines, magazines and more. – http://www.doosan.com/
EXTERRAN.	USA	3	O&G production equipment, natural gas compression and processing and produced water treatment solutions. – http://www.exterran.com/
Schlumberger	USA	3	Wide O&G services and products including seismic, drilling, completion, characterization, subsea and processing and separation. – http://www.slb.com/
SIEMENS Ingenuity for life	Germany	3	Diverse business including automation, building technologies, drive technology, energy, healthcare, mobility, financing and industrial services. – https://www.siemens.com/
vtip	USA	3	Affiliated corporation of Virginia Tech, they support the protection, marketing and commercialization of technology and innovation. – http://www.vtip.org/
ALKEM SOLUÇÕES ENERGÉTICAS E AMBIENTAIS	Brazil	1	Technology business focusing on the sanitation, industrial heating and biomass energy. – http://alkem.com.br/

5.2. Meso analysis

The Meso analysis for the Patents has some in common taxonomies with the papers, set on 4.2.1. For instance, ‘flotation type’ and ‘equipment type’ were also applicable for patents. However, due to the difference in the purpose of the documents, taxonomies linked to the contents on the papers as ‘research type’ and ‘main area of study’ were adapted to ‘invention category’. Similarly, ‘sector of application’ is modified to the ‘sector of player’ since many patents claim wide range of application, as mention before.

Alike the papers, a more detailed evaluation are done with some of the taxonomies by analyzing more specifics data, which correspond to the Micro analysis. The patent´s taxonomies are presented below followed by the results and discussions.

5.2.1. Taxonomy for the patents

With the classifications adjusted for the Meso analysis on the patent study, the taxonomy list it:

- Invention category: what is being patented, as equipment, method, system, chemicals, monitoring, etc.
- Sector of player: the area of application of the invention, established from the player sector. For instance, Oil & Gas, Water treatment, Mineral, etc.
- Flotation type: the type of the flotation process. For example, dissolved gas flotation, Induced gas flotation and electro-flotation. For cases where flotation process was studied for any application, it was considered as “general”.
- Apparatus type: the type of cell related to the invention. For instance, column, tank, electro-flotation cell, etc. For cases where the invention was not linked to a specific model, it was considered as “general”.

5.2.2. Invention category

The category evaluation of what is being invented confers an overview of the patent set profile, i.e., which kind of invention is predominant in the area of this study.

The American law governing patents specifies the main classes of subject matter of inventions or discovers (USP171), they are:

- Process – defined as process, act, or method, being the last one the term utilized in this work.
- Machine – that in this study is subdivided in equipment (after flotation equipment), component/part of equipment and monitoring tool/control device.
- Manufacture – which is composition of articles and referred in this work as 'system'.
- Composition of matter - related to chemical compositions.

The Table 15 shows the rank of the inventions in each of the bases, the sum and the percentage over the 68 patents. Many patents were classified with more than one category.

The most common invention type found for both INPI and USPTO was equipment, with a total of 39 patents considering it, which represents more than half of total. In second place also for both bases there are the methods type with 27 papers. In the third overall position comes the component/part of equipment with 10 papers. The last 3 are chemical(s); systems, which are apparatus with multicomponent; and monitoring/control tools.

Table 15: Invention category

Invention type	USPTO	INPI	Total	Percentage over total patents
Equipment	30	9	39	57%
Method	19	8	27	40%
Part of equipment	8	2	10	15%
System	7	0	7	10%
Chemical(s)	2	4	6	9%
Monitoring/Control	3	2	5	7%

Equipment was the main content of both papers and patents showing its importance for the research and business. As posted by Scholz (2006), the internal layout has considerable influence on the performance of the flotation unit. It is the core of the flotation process and it has space for innumerable designs, as already mentioned. Due to its importance there is a taxonomy dedicated to 'equipment type', on item 5.2.5.

Method, equipment components and systems are, to some extent, related to equipment itself. Chemicals and monitoring tools also appear on both bases but with different level of predominance.

It is interesting to observe a lower contribution on the patents development regarding Chemicals (6 documents – 9%) compared to paper results (23 documents -35%). It goes against the observation of Nagaraj, *et al.* (2016) in their study of the evolution of the flotation chemistry and chemicals. In this study, they stated that, keeping the trend from twenty years ago, still nowadays "*most of the commercially relevant innovations in flotation reagents and their application have come from industrial research*". One of the reasons for this divergence may be linked to the industry sector, once his work is focused to the mineral application. In addition, it shall be noticed that from the 23 papers comprising chemicals on its study, less than half this subject was the primary research target.

Example of equipment patents are the "Dissolved air-flotation type pretreatment apparatus", "Pneumatic flotation machine and flotation method" and "Process and machine for electroflotation and forced flotation" that are dissolved, induced and electroflotation type, respectively. Cases of patent of part of equipment are "Flotation machine rotor" and "Dissolved gas flotation pressure reduction nozzle" claiming a rotor and a nozzle, respectively to a mechanical/induced and dissolved flotation application. Example of document patenting chemicals are the "Composition and methods for improvement in froth flotation" that claims to lower required dosages of emulsifiers with the given additive and "Flotation aids and processes for using the same" that claim controlling surface wetting with the additive. Example of patent contemplating methods and monitoring scope is the "Methods and apparatus for the continuous monitoring of wear in flotation circuits", "Methods and device for monitoring the operation of flotation cell" and "Method of froth flotation control" that refers respectively to the monitoring of deterioration of components, froth speed and gas flow rate.

Micro analysis

Some equipment were described as optimization of prior art, which means there were patents of the same equipment with a new improvement in further (new versions) patent. Among the enhancements from patents of the same equipment there were: reduced footprint and power requirements, less components leading to less chances of failure and better structural integrity minimizing corrosion.

The equipment design was quite diverse. Some of the characteristics disclaimed on the patents are:

- Original variety or an improvement from previous version.
- Operated individually or in parallel/series with other apparatus.
- Multiple purposes rather than just de oiling, for instance, degassing function.
- Flexible machinery with adaptable parts to adjust to different scenarios as: option for vessel orientation, alternative bubble generation device, choice for inlet profile; or less flexible like: modular design and standard shipping container structure.
- Part of a system.
- Flow pattern, for example, rotation flow.
- Mobility/transport feature.

There were no single patents classified solely as method category. The patents declaring a method in general had as a primary purpose the claim of an innovative equipment, component, system, etc. Possibly because alongside with a new design, comes a novel procedure at some aspect(s). The methods reports were mostly referred as the way of using the invention, for example: “method for operating...” and/or the way to achieve an action by using the invention, for example: “method of improvement...”, “method for purifying...” method of extraction...” etc. A good case of patented method with the set of documents studied in this work were about a method and device for converting horizontal tanks into gas flotation separators where it presented manners of transforming existing equipment used for other function into flotation process application.

All the part of equipment were from components responsible for bubble insertion/spread. From the 10 patents, six were related to rotor, three to nozzle and one to an alternative sparging device. One of the nozzles had no information about the process and the other two were applied to the dissolved gas flotation. The rotor and sparging device were all applied to induced gas flotation, being the rotor evidently specifically the mechanical type. These data is consistent to the fact that IGF has many alternatives for bubble generation while in DGF the most important bubble formation is linked to the pressure drop, which results in less diversity for equipment components related to the bubble entry.

With regards the chemicals, 4 out of 6 were from the American company 'Ecolab' in the water treatment industry, disclosing chemicals to improve effectiveness of other additives such as collectors, frothing agents, regulators, depressors, deactivators, and/or activators. From the other two patents one was chemical additives to control surface wetting, hydrophobicity and surface forces in flotation process, and the other one was related to a monitoring process based on a chemical property. An evaluation of chemicals concerning the industry sector is presented on the Micro analysis of the 'sector of player' on item 5.2.3.

The monitoring solutions found in this study had general application and different characteristics. The controlled variables were: gas rate/recovery, froth speed, chemicals concentration, components wear and bubble size. Improvement in the controllability of the process increase the process efficiency, consequently enhance profit, quality and safety.

The systems patents were all within USPTO and, like the method, were also classified with other categories, and 6 out of 7 were from the dissolved gas flotation. Half of system patents were from the American corporation Sionix where the components were disposed in-line on a shipping container system. The arrangements included among others: conveyor belt, collection tanks, apparatus for skimming, decanting, filtration, screening, etc. In addition, there was a patent in which the system was composed of flotation process together with a biological treatment. This is another similarity of the patents with the papers work – both contained combination of process. It reaffirms the possibility of the flotation process being part of multisystem treatment. Moreover, the use of combined physic-chemical and/or biological treatment is supported and motivated from the literature as in Ahmadun, *et al*. (2009) work where this it is indicated for technology optimization of produced water treatment in order to comply with reuse and discharge limits.

<u>The International Patent Classification:</u>

The International Patent Classification (IPC) is a system of sorting inventions and their documents into technical fields covering all areas of technology. It was established by the Strasbourg Agreement 1971, and is used by the patents bases in a way to organize its documents. Every patent document is given a classification symbol by the examiner indicating the technology to which they pertain (WIP17).

As a way to complement and compare the profile of the patents, in addition to the analysis of category of the subjects, the inventions were also evaluated according to its IPC number. The results are presented on Table 16.

Table 16: IPC distribution

IPC code	IPC description	USPTO	INPI	Total	Percentage over total patents
C02	Treatment of water, waste water, sewage, or sludge	24	6	30	52%
B03	Separation of solid materials using liquids or using pneumatic tables or jigs; magnetic or electrostatic separation of solid materials from solid materials or fluids; separation by high-voltage electric fields	15	7	22	38%
B01	Physical or chemical processes or apparatus in general	1	3	4	7%
G01	Measuring; testing	1	-	1	2%
G08	Signaling	1	-	1	2%
	Total	**42**	**16**	**58**	**100%**

The general group - represented by the first letter of the symbol, utilized in this set are the following: group B is performing operations and transporting; group C is chemistry and metallurgy and group G is physics.

A clear majority of patents were classified by the bases as CO2 and B03 which characterize them respectively as water treatment and solid separation by liquid or by electric field. These classes together with B01 - that is more generic group of physical/chemical process - account for the category of equipment and its derivation and the chemicals due their final application. The G01 and G08, as per their description, are related to the monitoring category patents. These qualitative profiles are similar with the ones got from category evaluation. These numbers are functional for giving an estimated overview of the patents profile, and it useful for a quick analysis. However, it does not give a detailed output as the technological prospection does once it examines technically and deeper the patents one by one.

5.2.3. Sector of player

While for the papers the sector of application of the flotation research was defined based on the investigation aim, the patent information of area of application was taken by the player's business market due to the generic definition of most of the patents. A list with the main players and their business description was given on item 5.1.3.1. There were companies specifically applied to water treatment segment and others with extended market business like industrial conglomerates, in which water treatment was one of the corporation branch. Table 17 presents the list of the industries found on the patents assignees comprising each patent base USPTO and INPI, and the Figure 50 shows the pizza chart with the percentage over both.

Table 17: Assignee industry

Assignee industry	USPTO	INPI	Total	Percentage over total patents
Water treat.	9	4	13	22%
O&G	10	2	12	21%
Diverse with water treat. branch	5	2	7	12%
Mineral/Metal	6	1	7	12%
Innovation interm.	5	1	6	10%
No assignee/ Natural person	4	1	5	9%
University	1	2	3	5%
Energy	0	2	2	3%
Chemistry	1	0	1	2%
Power and automation	0	1	1	2%
Unknown	1	0	1	2%
Total	42	16	58	100%

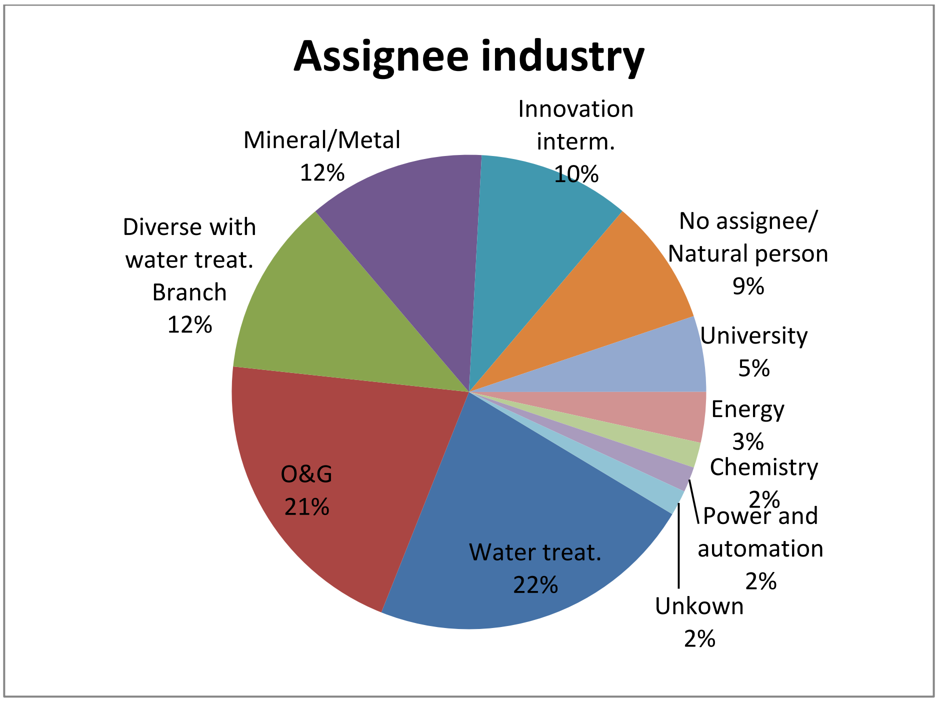


Figure 50: Assignee industry for the58 patents from USPTO and INPI

The players that contributed the most for patents of flotation process applied to oily water treatment within the last years had water treatment as their core business. They represent 22% of the total. The second most patent provider industry contributing significantly for the inventions is the oil and gas. Most of the players from this industry had broader business inside the O&G, including oil-water separation. The next in the rank of patents contributors originated from multiple segment corporations, including water treatment and enterprise from mineral industry.

There have also been markets not related to hardware supply. This is the case of companies specialized in the patent application services as consulting and/or registration, acting as an intermediate of companies and the patents base.

In addition, there were documents registered solely by natural person and universities. Other players with less contribution were from energy segment (excluding O&G), chemistry and power and automation.

Micro analysis

The Table 18 presents the data specifically from the main sectors for a more specific evaluation and comparison among them. The time series per sector comprising these main industries was presented before on item 4.1.1, Figure 46.

Table 18: Patents within water industry and oil and gas industry

Classification		Water Treat	O&G
	USPTO	9	10
	INPI	4	2
Process type	Dissolved	9 (69%)	2 (17%)
	Induced	1 (8%)	8 (67%)
	General	1 (8%)	1 (8%)
	Unknown	2 (15%)	1 (8%)
Patent category	Equipment	7 (54%)	12 (100%)
	Method	9 (69%)	4 (33%)
	Chem.	4 (31%)	-
	System	4 (8%)	-
	Part of quip.	1 (31%)	-
Equipment type	Tank	7 (54%)	4 (33%)
	Column	1 (8%)	1 (8%)
	CFU	-	3 (25%)
	Horizontal vessel	-	4 (33%)
	General/Unknown	4 (31%)	-
Main Players		Ecolab – 4 (31%)	Cameron – 4 (33%)
		Sionix – 4 (31%)	Schlumberger – 3 (25%)
		Veolia – 2 (15%)	Exterran – (25%)
		Others – 3 (23%)	Others – 2 (17%)

From the 13 patents belonging to water treatment companies, nine were from USPTO and four from INPI. From the USPTO ones, eight were of dissolved gas flotation type, and the remaining one was related to the induced gas flotation. From INPI, one was related to the DGF, one was general and the other two were unknown. This data shows a considerable predominance of dissolved gas technology to treat water compared to the induced gas flotation. The main players in this industry were 'Ecolab' and 'Sionix' with four patents each. Veolia contributed with two patents and three others the remaining documents. The most applied category of patents was the 'method' with 69% of total water treatment documents, followed by 'equipment' with 59%.

The oil and gas sector, differently from water treatment, had more patents related to induced gas flotation than dissolved gas flotation – 67% against 17%, which indicates the trend of technology in this industry. Another interesting output is that all patents were an invention of an equipment, in which tanks and horizontal vessels were the most common with four documents each, followed by CFU with three patents. Although column type has the benefits of small footprint, which is beneficial in an offshore facility, there was just one patent with this geometry. It shall be mentioned though, that CFU is a column based equipment, but considered as a specific model in this study. The main players in this industry were 'Cameron' with four patents and 'Schlumberger' and 'Exterran' with three documents each. Within the O&G, most of the applications were to the petroleum primary processing including bituminous sand processing. No focus to refinery was found on this study, suggesting that flotation process for this sector is more established and/or required less innovation compared to the petroleum primary processing.

There were four documents related to chemicals inside water treatment industry, out of the six from all patent list. None was from the O&G industry. It does not mean it is not an important aspect of the process in this industry. It is more comprehensive that companies that have expertise specifically in the water treatment have broader investments in elements related to this process such as additives; while the O&G industry, for having a wider business, may outsource part of attributes of their vast systems - that could be the case of chemicals.

5.2.4. Flotation Process type

The type of flotation process is an interesting information in order to see the dominance of each one in the last years concerning inventions. Many of them, mostly in categories of chemicals, monitoring and some of the components of equipment, were applicable to more than one type (or all) and were, therefore, classified as General. The Table 19 shows the results from individually USPTO and INPI and the sum of them, and the Figure 51 presents the pizza chart for each patents base.

Table 19: Flotation process type

Flotation process type	USPTO	INPI	Total	Percentage over total patents
Induced	22	3	25	43%
Dissolved	16	5	21	36%
General	4	2	6	10%
Electro-flotation	-	1	1	2%
Unknown	-	5	5	9%
Total	**42**	**16**	**58**	**100%**

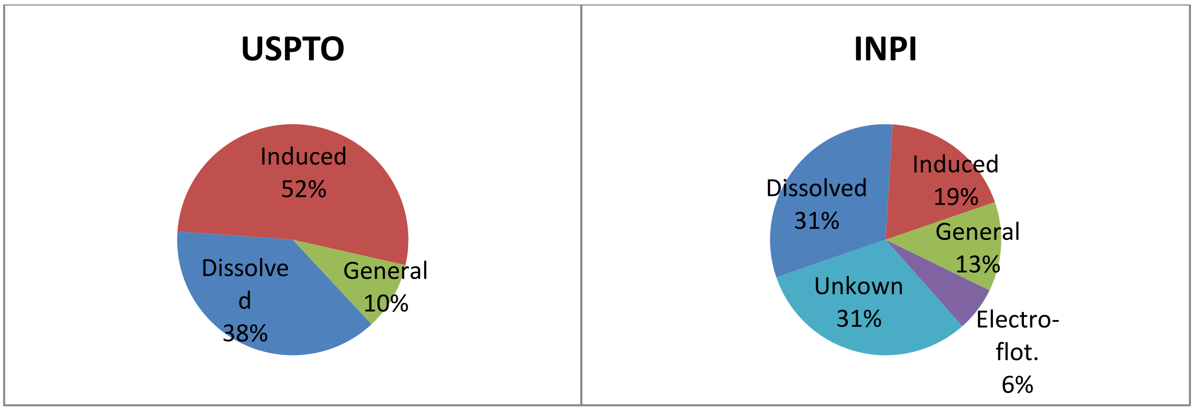


Figure 51: Flotation Process type within USPTO (42 patents) and INPI (16 patents)

The USPTO patents had clearer information of the inventions being possible to classify all. There were no invention related to electroflotation process type in this base, hence, the results were limited to three types: induced, dissolved and general. More than half were related to Induced gas flotation, 38% were associated to dissolved gas flotation and the 10% remaining applicable to both (general).

For the INPI results, due to the lack of information available for the patents, there were five patents (31% of INPI results) classified as unknown. Differently from the USPTO, the most known process type was the dissolved, with 31% (of INPI results). Induced gas flotation was the second most common known flotation type and there were, in addition, one patent related to electro-flotation process.

By analyzing the summation of the patents, as there were much more patents from USPTO than INPI, the profile go along with the American base. Most patents - 25 documents (43%) - are from the induced flotation type, followed by the dissolved gas flotation, with 21 patents (36%). These results are quite similar with the papers outcome that had 44% and 36% respectively for induced and dissolved process type, showing an alignment in the trend from the research and inventions in this regard.

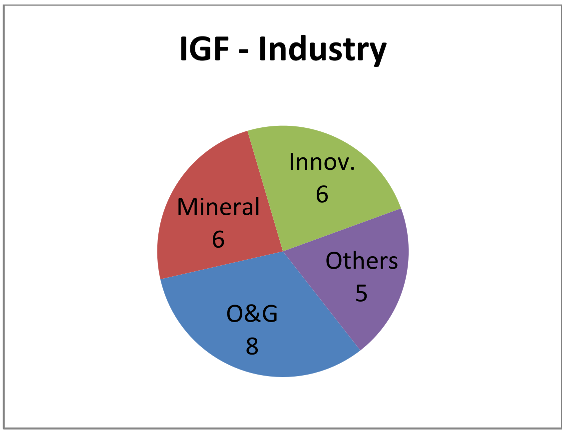
Same inference made for the paper´s study are applicable, i.e., both processes are the most common technologies, with the induced one having broader diversity of equipment. The same way, electro-flotation is not the traditionally applied for oily water treatment, but still there are front for its application.

Micro analysis

An analysis concerning specifically the induced type can be done by investigating its individual taxonomies. Figure 52 shows the industry and the invention type considering both USPTO and INPI.

The main industry sector is the 'O&G' with 32% followed by the 'Mineral' and 'Innovation' services with 24% each. This result has similar profile with the paper study considering the main industry there was O&G and the other two are not applicable to the papers studies as mineral related papers were excluded and intermediation is not pertinent.

The predominant invention category was 'equipment', representing 72% from all set, followed by the 'method' and 'part of equipment' with 32% and 28%, respectively. It is valid to mention again that a patent can have more than one category of invention. With regards the equipment type, 40% were specifically linked to the 'mechanical' principle, i.e., the bubble are dispersed by means of blades rotated by an electric motor.



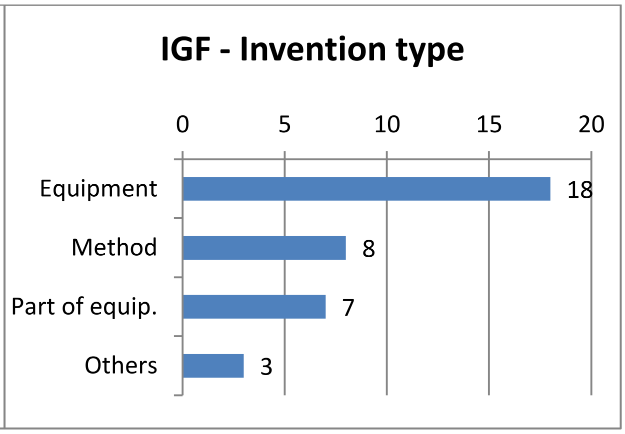


Figure 52: Industry and invention type within induced gas flotation (both patent bases)

With regards players, 24 out of 25 documents were from companies. Three of them are responsible for 48% of all the induced gas flotation patents, as can be seen on Figure 53. These are: 'Outotec Oyj' with 20%, 'Cameron' with 16% and 'Virginia Tech Intellectual Properties' with 12%.

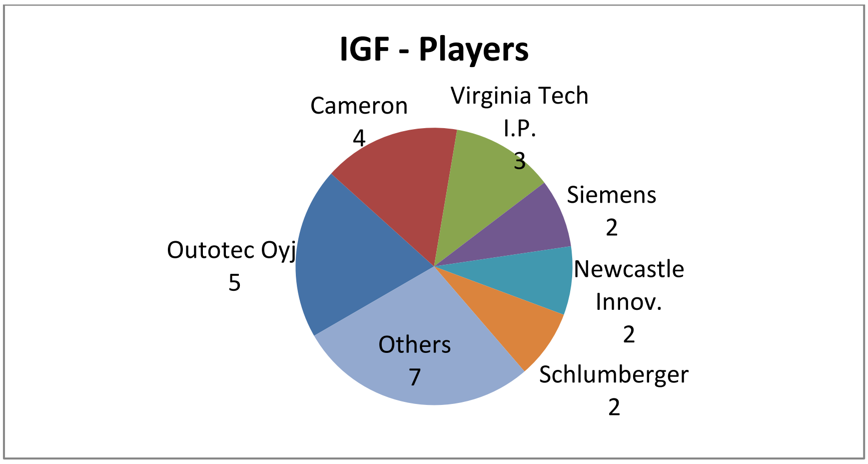


Figure 53: Main players within induced gas flotation (both patent bases)

Regarding the dissolved gas flotation, the micro analysis shows some divergences and similarities compared to the IGF, as can be seen on Figure 54. The main industry in this flotation type, responsible for 43%of the patents is the 'water treatment' application which means a generic treatment of water, followed by 'diverse' with 14% that represents companies with wide business area including water processing. Although this data may seem different from the papers results, it has areas that are nonspecific/general that may be applicable to many industries.

The major type of invention on DGF, like the IGF, is the 'equipment', representing 71% of the patents. 'Methods' and 'systems' were the next two most invention type with 43% and 29%, respectively. The patents comprising systems were nearly all from the dissolved gas flotation, and many of them had in common the modular, sometime mobile, unit. It is interesting to verify the profile difference between patents and paper contents. While the paper had major focus on the chemical usage, there were no patent considering additives. Another interesting output is that it was found one patent in the DGF that the bubble was generated by means of vacuum.

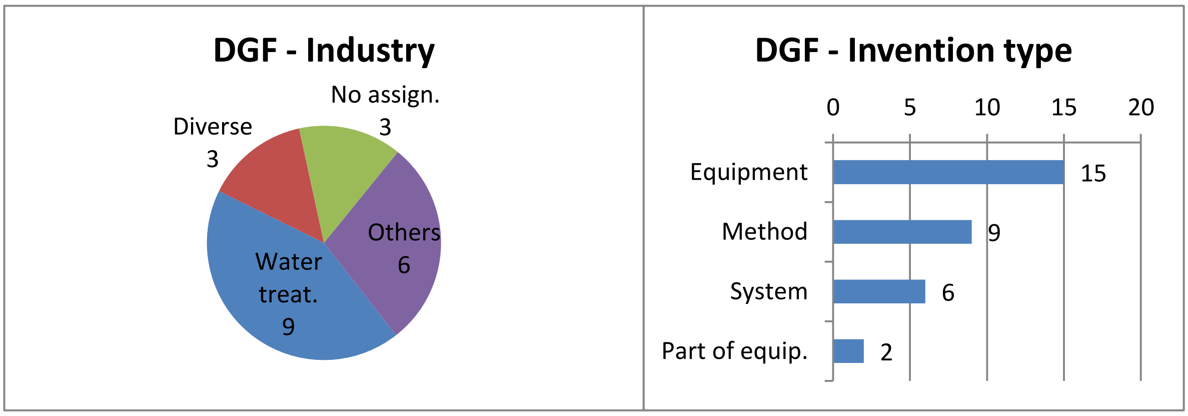


Figure 54: Industry and invention type within dissolved gas flotation (both patent bases)

The main players from DGF is shown on Figure 55. The two companies that stands the most in this process type are the Sionix Corporation and Doosan, with 19% and 14% respectively.

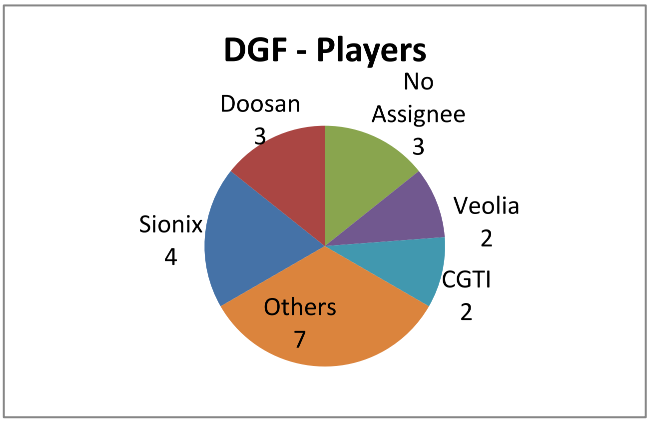


Figure 55: Main players within dissolved gas flotation (both patent bases)

It is interesting to compare the results from this work to a Russian patent study made by Eskin, et al.(Eskin, et al., 2015) specifically to the dissolved air flotation to the same application retrospective of 15 years with more than 120 patents from 20 countries. In that work it was highlighted three main trends among the patents: i) Treated fluid aeration time, ii) Combination with other purification method and iii) Improving the release gas stage distribution uniformity as shown on Figure 56.

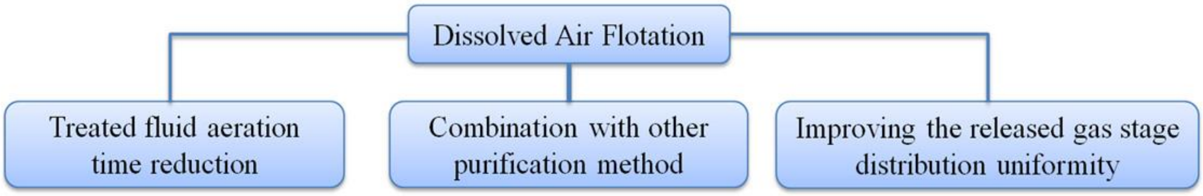


Figure 56: Modern dissolved air flotation development trends from Eskin´s study. Source: (Eskin, et al., 2015)

Differently from Eskin´s output, the time reduction was not a spotlight among the patents from this current work with DGF. The combination with other methods was found in this work but less expressive compared to other characteristics. And likewise the Russian results, the gas distribution improvements was also a central output in this study associated to the innovative equipment design and nozzles.

It shall be noticed that, although there is an overlap of years, that work comprises mostly distinctive period, it also considers further patent bases (ESPACENET, USPTO and RUPAT - the Russian base) and the methodology of work is not detailed. The divergences demonstrate that interest and trends within an area of study is directly related to the region and historical period. In spite of everything, the in-common attention to the gas distribution feature on both work can be inferred as being of great important general trend inside DGF.

5.2.5. Apparatus type

Apparatus report on the patents had much more details on its documents description than the publications from the paper study. In some cases in the papers, the apparatus itself was characterized by its bubble generation device rather than its geometrical shape as it was the only information available. On the other hand, although the patents had good description of the apparatus, they were not much related to a specific model. Most of the apparatus were described generically, different from the papers where some specific types of units where researched. The list of the apparatus found in the patents evaluation from both bases is presented on Table 20.

In general, columns and tanks were the main shapes from the devices researched by papers and registered by patents. Like the papers, in some way, it is partially because of the generically usage of these names. It is interesting to find a significant number of horizontal vessels in patents (5 documents), while none were specifically cited in papers.

With regards specific model of apparatus, the compact flotation unit was the one with more incidence - three documents, in which one of them it was inferred by the description and company portfolio, as the name was not directly given. Two other particular shapes where found: one based on a longitudinal pipe and other designed with an inclined plate. Only one electro-flotation cell was found.

The cyclonic static micro-bubble flotation column (FCSMC) highly incident on the paper study didn´t appear on the patents probably for being linked to a Chinese affiliation, which the country was not present on the patent list of this study. In addition, this apparatus type seems to be in the beginning of its development, so further outputs may become future innovations.

Table 20: Apparatus type

Apparatus type	USPTO	INPI	Total	Percentage over total patents
Tank	17	6	23	40%
General	10	3	13	22%
Column	6	1	7	12%
Horizontal vessel	5	0	5	9%
CFU	2	1	3	5%
Electroflot. Cell	0	1	1	2%
Particular design – Longitudinal pipe	1	-	1	2%
Particular design – Inclined plate	1	-	1	2%
Unknown	-	4	4	7%
Total	**42**	**16**	**58**	**100%**

With regards the bubble generation device, 11 documents (19%) were made by means of mechanical rotation and 10 (17%) by using an ejector/venturi tube. There were also five patent considering cyclonic flow pattern as a solution for improving performance. As an overall content, both papers and patents enclosed rotational flow pattern and bubble generation by venturi and rotor (mechanical), which indicate they are features with prominence on the process improvement in the last years, and therefore, a potential trend.

Micro analysis

The tank type of apparatus was distributed in the fallowing way with regards process type: 15 were linked to the dissolved gas flotation, six to the induced gas flotation and two general or unknown. Assignee type and sector as well as patent category were diversified.

All of the columns were from companies patenting apparatus. Most of them were applied for the Induced gas flotation process. The sectors of industry were varied.

All the companies related to the horizontal vessels were from the oil and gas industry, there was in addition one patent with no assignee. Moreover, all these patents were from USPTO base.

All three CFUs were patented by Schlumberger, which means they are also from O&G sector. The only electro-flotation cell got in this study was patented by a Brazilian company – 'Alkem Equipamentos Industriais', as mention before, the only Brazilian company found in this work. They attribute the gains on its developed equipment based on the automatically substitution of the electrodes.

5.3. Conclusion from patents

A set of 58 patents from the American and Brazilian patent base were analyzed, respectively, USPTO and INPI. Their profile can be summarized as mostly being related to the invention of an equipment or its variations as specific component or a full system. Most of them were generically described as a column or tank. Among the vast sort of particularities of design and features there were structural gains, flow pattern, flexibility, mobility, multiple functions, relation with upstream/downstream systems, etc. Chemicals and monitoring tools were also present among the patents but less relevant compared to the papers output.

The compact flotation unit was the specific apparatus model with more incidence. Its small footprint is advantageous for constrained zones like the off-shore area. Horizontal vessels were also encountered among the apparatus type, differently of the papers, where none was found (do not named alike at least).

Considering both patents base, the majority of the innovations were within the induced gas flotation technology, in which a good number of it was from the mechanical type. Nevertheless, companies specifically from the water treatment sector were mostly linked to the dissolved gas flotation. Only one patent was found for the electro-flotation, coincidently, the contribution of the only Brazilian company in the patent set list of this work - the 'Alkem Equipamentos Industriais'. There were, however, contributions from other types of Brazilian assignees (universities and institutions) that made Brazil the most relevant country on its national patent base – INPI. The main overall contributor country for patents was United States.

The sector with more innovation with flotation process were the O&G and water treatment. As expected, companies were the main type of assignees. Expressive players were the Finnish 'Outotec Oyj' of the mineral industry and the American companies 'Cameron', 'Sionix' and 'Ecolab' from the oil and gas industry and water treatment business.

5.4. Comparison between papers and patents

It is interesting and useful to compare the results from papers and patents. A patent is typically a final stage of a research processes (usually reported in scientific papers), i.e., in order to come up with an actual product, a series of investigations and tests have to be performed. Therefore, the characteristics and proportions of what has been studied compared to what actually became a product gives an additional output. This evaluation may, for instance, indicates future possibilities from researched aspects that were not found significantly in patents. It can also reinforce characteristics with similar profiles in both groups. Moreover, this comparison evidences qualities inherent of each community (research and industry). To help in this evaluation the results were summarized on Table 21 where some data and taxonomy from both are set (adapted when needed) side by side.

Table 21: Summary for comparison between papers and patents results

Data or Taxonomy (paper/patents)		**Paper**	**Patent**
DOCUMENT SOURCE		Science Direct Scopus	USPTO (American base) INPI (Brazilian base)
TOTAL DOCUMENTS		68	58
MACRO ANALYSIS	TIME SERIES	Oscillated through the year.	Oscillated through the year.
	COUNTRY	TOTAL 19 Top 4: China, Brazil, Canada, USA	TOTAL 12 Top 3: USA, Brazil, Finland
	AFFILIATION/ASSIGNEE TYPE	TOTAL 81 University 97% Institution 26% Company 22%	TOTAL 28 Company 81% Institution 5% University 5% No assignee/ Natural person 9%
	MAIN PLAYERS	China University of Mining & Technology - 8 Beijing Institute of Petrochemical Technology and Sinopec - 5 UFRGS, UFRGN, Chulalongkorn Univ and Univ. of Queensland - 3	OutotecOyj - 5 Cameron, Sionix and Ecolab - 4 Doosan, Exterran, Schlumberger, Siemens and Virginia Tech IP - 3
MESO ANALYSIS	FLOTATION PROCESS TYPE	Induced 44% Dissolved 35% Electro 7% General 9% Unknown 10%	Induced 43% Dissolved 36% Electro 2% General 10% Unknown 9%
	APPARATUS TYPE	Column 18% FCSMC 12% Tank 10% CFU 9% General 22% Loop flot. Cell 7% Electroflot. Cell 7% Others30%	Tank 40% General 22% Column 12% Horizontal vessel 9% CFU 5% Electroflot. Cell 2% Others 11%
	SECTOR OF APPLICATION/PLAYER	O&G 41% General 44% Others 15%	Water treat. 22% O&G 21% Others 57%
	MAIN AREA OF STUDY / INVENTION CATEGORY	Related to equipment 56% Chemical(s) 35% Related other equip./process 22% Model 21% General 10% Monitoring/Control 4% Other 3%	Equipment 57% Method 40% Part of equip. 15% System 10% Chemical(s) 9% Monitoring/Control 7%
	RESEARCH TYPE	Experimental 79% Review 12% Simulation 5% Sim. + Exp. 4%	-

Few more documents were got on the paper set compared to the patents one, considering the chosen sources in this work and the selection/filtering process. With regard to the historical distribution, both oscillated the quantity of document per year, making it difficult to analyze growth tendencies. However, the number of researches comprising the word “flotation” on title and/or abstract, which considers the application of flotation in any area, showed a progressive increase profile.

The in-common country with more incidence was the USA. Brazil appeared in both groups because of its patents base – INPI – as it was not in the USPTO list. Yet, it was a key contributor for scientific papers together with China, which in turn, did not appear on the patent list. However, a small overview on the European patent base – ESPACENET – showed a major presence of this country within similar search, which indicates that the disparity is related the geographical region, and not for the lack of patent applications. While Science Direct and Scopus take publications from all around the world, the patents base are selected as per the interest of the organization in the corresponded region. Prominence of countries in paper is believed to be related to the mineral industry, whereas in the patents it is partially related to the location of the base.

With regards the number of organizations providing developments, papers presented a huge total affiliates (82) due to the multiple partnership characteristics of researches, while patents had almost 3 times less contributors (28), as typically only one is set as assignee. The type of affiliation/assignee reflect the characteristic of each group. Universities are typically more interested in academic investigations requiring several researches that are published in the format of scientific papers, while companies’ developments are habitually focusing on industrial application, which is predominantly registered as patent. This explains the greater proportion of universities contributing for papers and the higher involvement of companies with patents. The affiliations/assignees with more production were set as main player, and each group had different organizations. There were only two organizations appearing in both papers and patents list: the company Siemens and the university UFRGS (Universidade Federal do Rio Grande do Sul). The developments, however, do not seem to be from the same subject. Table 22 shows the documents for both organizations to both groups. As can be seeing, Siemens paper is related to a CFU equipment while the patents descriptions do not refer to this type. Similarly, the only UFRGS patent was about a monitoring device that was not mentioned in the 3 papers from the same affiliation. It shall be reinforced though that not all information was available.

Table 22: Siemens and UFRGS documents for Paper and Patents

Affiliation/ Assignee	Paper	Patent
Siemens	Performance analysis of a novel CFU	Nozzle, equipment and methods of a flotation system (INPI)
		Sparging device for a flotation cell (USPTO)
		Pneumatic flotation machine and flotation method (USPTO)
UFRGS	A short overview of the formation of aerated flocs and their application in solid/liquid separation by flotation	System for measuring, monitoring and control bubble size in column flotation (INPI)
	Modified jet flotation in oil (petroleum) emulsion/water separations	
	Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles	

The flotation process type among both papers and patents appeared is a very similar proportion, as presented on Table 21. IGF represented 44% and 43% of the process type in the documents respectively for papers and patents, while DGF represented 35% and 36%. This similarity may represent the overall usage predominance of such technologies to treat oily water, with the IGF the mostly applied type. Both groups had small presence of electroflotation developments also related to the (minor) usage of this technology in this application. The fact that the set of paper had more documents related to the electroflotation than the patents set evidences the upper proportion research/innovation. As posted before, this may imply future trends in the application of this flotation type, depending on the success of the current research efforts.

The apparatus type evaluation is more valuable for comparing specific models, as tanks and columns are commonly named after generic geometries. With this regards, only the compact flotation unit appeared in both groups, which reinforcing its trends. The high percentage of FCSMC on the paper that was not found on patent study maybe in reason of its initial development process and/or due to the fact that it is from a Chinese origin – country not found on the studied patent bases. Horizontal vessel, on the other hand, was just found on patents. The foremost interest in this type from the corporation side (major assignee of patents) is possibly related to its advantage in industrial application. Horizontal vessel can provide a strong structure which is convenient for handling harsh atmosphere/fluids; it has a standardized and stablished production way, it has mobility advantages and it can be converted from/to other applications, which make it a good casing solution for flotation cells. Its internals configuration are the main keys in the process efficiency, being the focus of developments.

The application of flotation process in treating oily water was notorious for the oil and gas industry in both groups. This outstanding is understandable as it produces enormous volumes of waste. Apparently, among oily waste generators, O&G seems to be the one concerning the most. It shall be noted, then, that in patent analysis, the sector was set by the business of the assigned company because most of patents claimed wide range of application of their innovations; while in papers the sector of application was set by focus of the study. This explains the high incidence of generic water treatment sector in the patent results.

The scope of each paper and patent was mainly the development of equipment. The similar results between both strengthens this output and shows that main efforts are aiming equipment improvement. Although with different proportions, chemicals and monitoring tools also attracted interest showing their importance in the system.

6. CONCLUSIONS

Gas flotation has showed to be an efficient alternative to treat oily wastewater, which has rigorous discharge limits set by regulation agencies worldwide. The diversity of effluents and the dependence on many variable result in a major need for research and development.

The technological prospection of papers from Science Direct and Scopus databases and the patents from the USPTO - United States Patent and Trademark Office – and INPI - *Instituto Nacional da Propriedade Industrial* (Brazilian patent base), with regards the flotation process on the treatment of oily water over the years 2010 – 2017,provided an overview of research and innovation developments and trends in this area.

Among the studied taxonomies, papers and patents showed some similarities, that reinforce general tendencies and characteristics of the process, and divergences related to the profile and interest of each community.

The process type more commonly associated with the developments were the induced and dissolved gas flotation, corroborating the literature report of both processes being the two most applied flotation techniques. The results from both groups were similar with 44-46% of IGF incidence and 35-36% of DGF. One of the possible reasons linked to the slightly larger amount of developments in IGF technology is the broader range of different devices. For instance, there are several alternatives for bubble sparging system in IGF, which lead to a wider window of studies. Regarding IGF, the mechanical type was the most frequent. Bubble handling by rotor (mechanical) and venturi were more frequent, which indicate they are (still) notorious features on the process improvement in the last years. Therefore, it should be possibly kept as trend. The DGF was the most associate type inside the general water treatment companies, and the gas distribution feature a key attribute.

Although less expressive, it was interesting to find developments on the electro-flotation process applied to the oily water treatment once it is currently not traditionally the field of application of this type due to hydraulic loadings and cost barriers. As a patent is typically a final stage of a successful research process, upon further findings in researches related to elctroflotation, this could become a future growth in patents related to this technology.

The countries with more contributions for the papers were: China, Brazil, Canada, and United States. A study showing installed flotation columns per country on the area of mineral processing portrayed similar profile of the papers publication. Therefore, the hypothesis for having these countries standing out the researches could be related to the mineral industry. Existing research centers focusing the flotation applied to the mineral sector might have extended its studies for oily water treatment due to the growth of oil and gas industry in the last decades, together with the environmental growing restrictions.

The countries with more documents within the two patent bases were US, Finland and, for the case of INPI, Brazil. These results came from the substantial patents application of some companies from these countries. In the case of Brazil, the assignee profile varied from institution to natural person, with the contribution of only one company: ‘Alkem Equipamentos Industriais’ –a corporation with diverse business with water treatment branch.

The main sector of application concerning this study was the O&G industry. Companies on the general water treatment business also highlighted in the patents contribution.

The main players for the papers were the Chineses ‘China University of Mining & Technology’, ‘Beijing Institute of Petrochemical Technology’ and ‘Sinopec’. The Brazilian affiliation with more publications was ‘Universidade Federal do Rio Grande do Sul’. Within the patents, the players with more documents were the Finnish ‘Outotec Oyj’ from the mineral sector, and the American companies ‘Cameron’, ‘Sionix’ and ‘Ecolab’ from the oil and gas industry and water treatment business.

Apart from the general columns and tanks, the apparatus model with more research on the paper evaluation was the cyclonic state micro-bubble flotation column (FCSMC). A highly incident model in both papers and patents analysis was the compact flotation unit (CFU). Both are relatively new models useful for space restricted areas such as off-shore facilities.

The rotational flow is considered a trend of flow pattern once several equipment were making use of centrifugal force for improving process performance, and researches were investigating this system hydrodynamics. Chemicals and monitoring tools, adjunctive in the process, were also present on both papers and patent, but less expressive in the last one.

The influence of operational parameters and design improvement of equipment were the main area of research of the papers, being the gas rate the most researched variable. Likewise, the major patent category was related to the development of a flotation equipment. It was found a considerable diversity of elements and/or design among the equipment. The results show up the diversity of alternatives and complexity in this process. Due to the wide possibility of bubble generation, flow pattern, equipment geometry and extensive physic-chemical parameters involved in flotation process, it has a considerable window for studies and enhancements.

Although flotation exists for a long time, the number of studies regarding flotation in general has increased continuously in the last years (2010 – Jul 2017), which shows still increasing interest from the research community in this process. However, a wider time series window is required to verify the tendency concerning specifically the application in the oily water treatment, as the profile obtained in this study showed oscillation.

The profile of the outputs obtained from this technological prospection are considered valuable for strategic organizational planning and management, and suggests good perspective for the application of the flotation process in the oil containing wastewater treatment, as per the produced water treatment.

7. SUGESTION OF FUTURE WORKS

For future works, other areas, emphasis, taxonomies, and window can be applied. Some suggestions of further works are listed below:

- Consider a wider range of historical period, comprising for instance 10 – 20 years, in order to have a broader overview and consider older trends;
- Contemplate other documents sources, as the European patent base ESPACENET. Regional characteristics may outcome comparing different sources. Moreover, R&D development from companies may be farther encountered in fairs or specific communities such as the SPE – Society of Petroleum Engineers;
- Adopt other key words combination to evaluate possible extra characteristics. For instance, do not restrict the content with the word <oil> to comprise generic studies as process mechanisms;
- Provide the technology roadmap analysis to come up with market and business useful data to enhance management planning;
- Consider other taxonomies as a specific classification or parameter of interest, for example, bubble size range (adapting the study accordingly).
- As per further areas of interest, specific applications of flotation process can be considered in addition to oily water treatment;

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