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Common strategy to prevent the Danube's pollution technological risks with oil and oil products - CLEANDANUBE

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STUDY 3

Study on possible constructive variations, technological implications. Complete project theme

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COMOTI
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ABSTRACT

This stage consists in developing several possible constructive variants according to the preliminary project's theme, analyzing concomitant the technologic implications. Such activity is very complex because it has a multidisciplinary character (chemistry, material sciences, fluid mechanics, fluid flows in machines with rotating blades, oppositions of materials, etc.). This activity will conclude with a final project theme, to achieve the objectives of the project.

Romania and Bulgaria are two important countries in the Danube Basin, both from the surface and population point of view, and, therefore, have a significant impact on the river

The ecosystems of the Danube River Basin are highly valuable in environmental terms and support a large number of economic and social activities.

In order to create a common structure for checking and managing Danube pollution, in the frame of this project, Romanian and Bulgarian specialists and researchers have began to perform tests for evaluating the quality of Danube water. These joint technical efforts will help in protecting the environment and to find efficient solutions for cleaning the oil products from polluted water.

Therefore, on 29 June 1994, the Convention on Cooperation for the Protection and Sustainable Use of the River Danube (Danube River Protection Convention) was signed in Sofia. Since 2000, the ICPDR has also been the coordinating body for implementing the EU Water Framework Directive (WFD) — the legal mechanism for managing water in the European Union. During more than 15 years of existence, the ICPDR has established a number of products and tools which support joint activities and sustainable development. One of the most important early achievements was the Transnational Monitoring Network (TNMN), managed by the ICPDR on the basis of national monitoring stations. This provides information on the ecological and chemical status of Danube basin waters.

Chemical compositions and physical diversity of the estate of petroleum products, which may be potential pollutants, needs to remove their effects and design effective technology adaptable to specific conditions.

For this reason, using a mobile laboratory to determine in a short time the physical and chemical properties of pollutants and based on their schedule to the optimum functional parameters of the centrifuge plant.

These parameters will be determined both by calculation and by simulating the process of separation using CFD (Computational fluid dynamics).

As a result of the numerous working conditions, imposed by the raw material and the resulted products, it was built many types of centrifuges.

Due to specific particularities of the technology that we intend to implement, on removing the effects of oil pollution to the Danube, Romanian and Bulgarian partners must implement a common strategy to pursue these issues:

- Water-quality monitoring and pollution hazard identification;
- Limiting pollution-expansion effect;
- Removal effect by the recovery of pollutants.

For this reason, on both banks of the Danube, water quality monitoring stations to be able to identify in short-time phenomenon of pollution and prevent its spread. One way to avoid extending the effect of pollution is to install protective barriers which hold pollutants that will subsequently be recovered by the proposed technology.

3.1 Study on possible constructional versions

3.1.1 Separation modes and centrifugal types

As a result of the numerous working conditions, imposed by the raw material and the resulted products, it was built many types of centrifuges.

Tabel 1 gives a centrifuge classification by the effectiveness factor z(see chapter 2.3.1 study No. 2) , and in Fig. 1 a systematization of the centrifuge types from combining the different classification criteria.

Tabel 1 Centrifuge clasiffication

Classification criteria	Clasiffficatrion groups
Separation power(eficcience factor z)	Normal Centrifuge (z<3000) Supercentrifuge (z>3000) Ultracentrifuge ($z>5\cdot10^5$)
Centrifugation purpose	Filtering the granular or crystalline suspensions Suspensions sedimentation Emulsion separation
Function	Discontinuous (in batch) Continuous
Download (precipitate evacuation)	Manual By gravitation, at low speed With pulsed pistons With spiral conveyer With knives and scrapers By centrifugal force Hydraulics
Axis position	Vertical Horizontal Oblique
The support of the centrifuge	Suspended Supported
Operation	Upper Lower

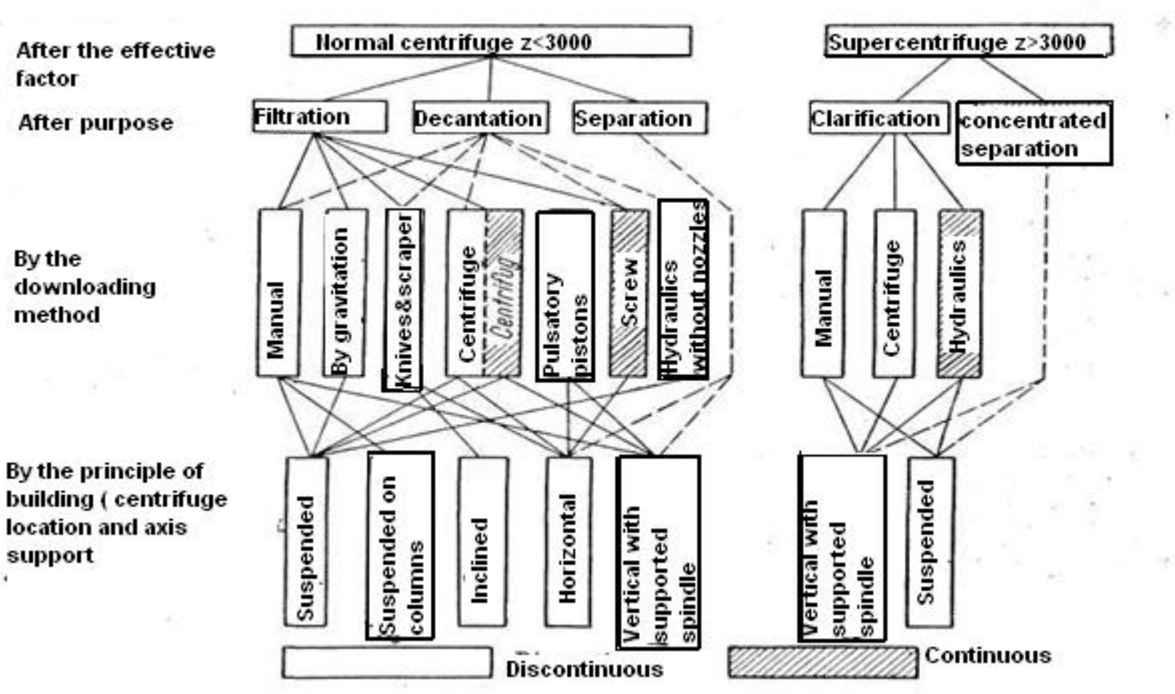


Fig. 1 Filltrating Centrifuges

These centrifuges are characterized by a perforated brake drum, lining with mesh or cloth. They serve to filter suspensions, separation of crystals from initial solution, drying the textiles.

Filtering Centrifuge with discontinuous function

With these centrifuges are working in batches. They are built ussualy with vertical axis.

Batch filtering centrifuges with manual discharge

The cycle of these centrifuges has the following phases: load; start and acceleration up to speed regime, centrifugation itself, washing of the precipitate, discharge, braking till stop, unload.

The brake drum of these centrifuges is fixed on the vertical shaft, rotated through a belt or by a electrical drive. The brake drum is perforated and reinforced with resistances circles. The bottom of the brake drum has a small declination to the periphery.

An annular cap covers the portion where the precipitate layer is formed. The brake drum in surrounded by a cylindrical cover, to capture the filtrate and prevent accidents. A pipe with sprinkler serves for washing the precipitate (crystals). The precipitate's discharge is done manually after the centrifuge stops and the cover is opened.

These centrifuge are indicated for separating suspensions that needs o long period for centrifugation and washing. The optimum efficiency factor – z is determined experimental, taking account the inconveniencies of a to big z: the decrease of the precipitate's permeability; slow discharge of the to much compacted precipitate.

Sedimentation centrifuge with horizontal screw.(Fig.3)

The brake drum, with a ratio L/D = 1,5 ...4, is built: a) conical or cylinder-conical, with long coneand short cylinder, for heavy particles suspensions, leading to a low humidity sedimentation; b) cilinder-conical, with long cylinder and short cone, for fine particles; c) cilinder-conical with the cylinder .equal to the cone

In general it is used the L/D>2,2 to separate suspensions with average and high concentrations (L – total lenght of the brake drum; D – it's maximum diameter). to separate the components fron the residual waters it is used L/D=4, with the lenght of the cone portion equal to1/3 from total lenght.

The tip cone angle is generally 10 …15^o. The screw is done with one or two beginins. There is a speed difference of 0,6-4% between screw and brake drum. The relative speed must be tuned with the solid phase content of the suspension.

For the centrifuge used to separate the components of the waste waters, good results were obtained with relative peripherical speed of the screw, in relation to brake drum of 0,15...0,18m/s. In general, the directions of rotation for screw and brake drum are the same.

There are built centrifuges with fast screw or with slow screw. The fast ones have smaller relative diameters (160...180mm) and big separation factors (1800...3500), where the slower ones have bigger relative diameters (900...1800mm) and average separation factor (350.. 600).

The suspensions whose humid solid phase form a sticky mud, which stick to the screw spirals, is very hard to work with on these centrifuge.

At a centrifuge working in countercurrent (fig. 2), the suspension feeded through pipe 1 goes through the A openings of the screw body, into the screw channel, in the passing section from cylinder to cone. Sedimentation occurs due to centrifugal force. The sediment is transported,because relative speed of the screw, to the smaller diameter evacuation end, where gets out from brake drum through te openings B, in case 7, and the filtrate goes to the oposite end(in countercurrent) where exit through brake drum, openings 5, in the case 6. The discharge openings can be radial or axial, fixed on cap C.The radial position of opening 5 can be adjusted through caps: modifying the inner diameter of the liquid ring, and consequently, the lenght L_{sed} of the sedimentation zone. By increasing lenght L_{sed} shrinks the lenght of the drainage sedimentation zone L_d.

To wash of the sediment (when neccesary) are used pipe 14, from which the washing water passes through the small diameter holes E into the screw channel. The filtrated dillutes because of the washing, and is removed through the openings.

The spire of the screw force the filtrate to move on the direction of the screw channel (prevents the direct axial flow of the liquids toward spillways), on a longer way, which favors the sedimentation. Along L_d zone the sediment is drained through filtration and compacted.

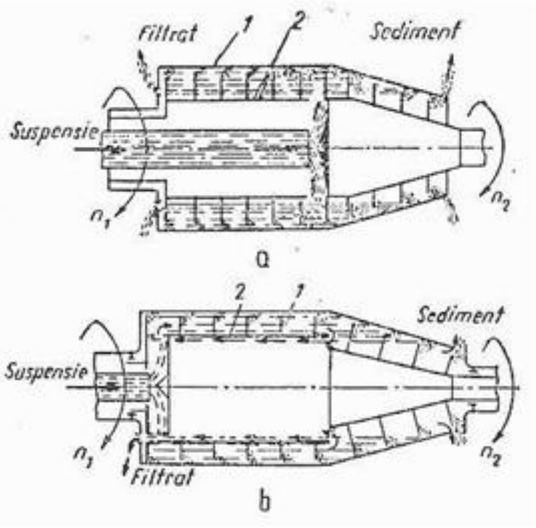


fig. 2 Screw centrifuge functioning sketch:

a) – in counter-current;

b) – in echi- current.

In some builds it were achieved good results by combining the plain brake drum with a portion with holes.

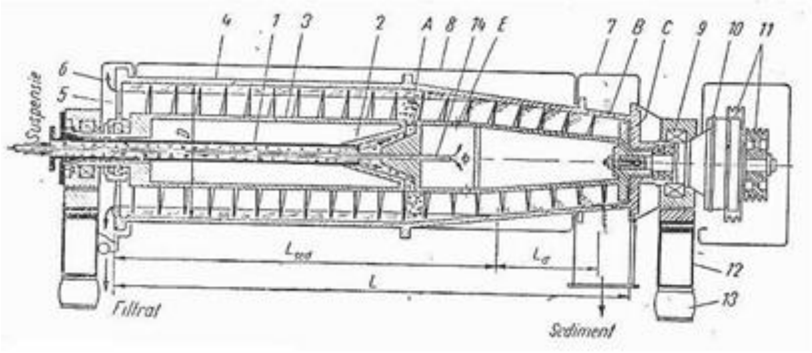


Fig. 3 Cross section through a sedimentation screw centrifuge.

In fig. 3 are presented the screw, the brake drum and the case of the centrifuge, and the technical characteristics of some sedimentation screw centrifuge produced by **FLOTTWEG AG** are given in tabel 2**.** Centrifugal separators for liquid-liquid phases of different densities and solid phase are known in the literature like **TRICANTER.**

This range the three phase separation is approaching most our application but are used for oil recovery from lagoons and sedimentation ponds,where the concentration of solid phase is high.

The FLOTTWEG TRICANTER enables three-phase separation,i.e. the simultaneous separation of two immiscible liquids with different densities and one solid phase, provided that the solid phase is the heaviest phase. The most important difference from a decanter is the separate discharge of the two liquid phases.

The FLOTTWEG TRICANTER discharges the heavy liquid through an adjustable impeller under pressure and the light phase by gravity. The adjustable impeller allows adjusting the separation zone and degree of separation within the machine during operation. This optimizes purity of the liquids and may possibly eliminate downstream equipment.

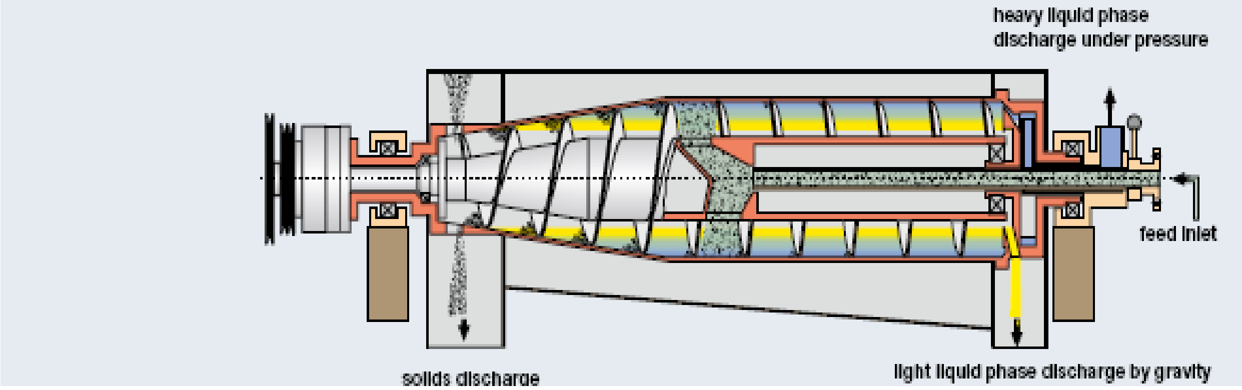


Fig. 4 FLOTWEG TRICANTER(THREE PHASE DECANTER)

Tabel 2 Technical characteristics of

FLOTTWEG HTS DECANTERS for sludge dewatering

Type	**C3E-4**	**C4E-4**	**C5E-4**	**C7E-4**	**Z92-4**
Material of construction	All product wetted parts are made of high grade stainless steel				
Dimensions					
Lenght	2980 mm	3520 mm	4100 mm	4800 mm	5740 mm
Width	940 mm	1140 mm	1520 mm	1720 mm	2780 mm
Hight	900 mm	1030 mm	1210 mm	1400 mm	1730 mm
Gross weight	1700 kg	2550 kg	4700 kg	8700 kg	16200 kg
Motor for bowl drive	18,5 kW 5 hp	22-37 kW 30-50 hp	45-75 kW 60-100 hp	90-132 kW 125-200 hp	160-250 kW 250-350 hp
Motor for scroll drive	4 kW 5 hp	7,5 kW 10 hp	15 kW 20 hp	30 kW 40 hp	30-45 kW 40-60 hp
Feed capacity	10-20 m^3/h	20-40 m^3/h	30-60 m^3/h	60-120 m^3/h	90-180 m^3/h

3.1.2 Definition of operational schemes for removing the effects of water pollution

Due to specific particularities of the technology that we intend to implement, on removing the effects of oil pollution to the Danube, Romanian and Bulgarian partners must implement a common strategy to pursue these issues:

-Water-quality monitoring and pollution hazard identification;
-Limiting pollution-expansion effect;
- Removal effect by the recovery of pollutants.

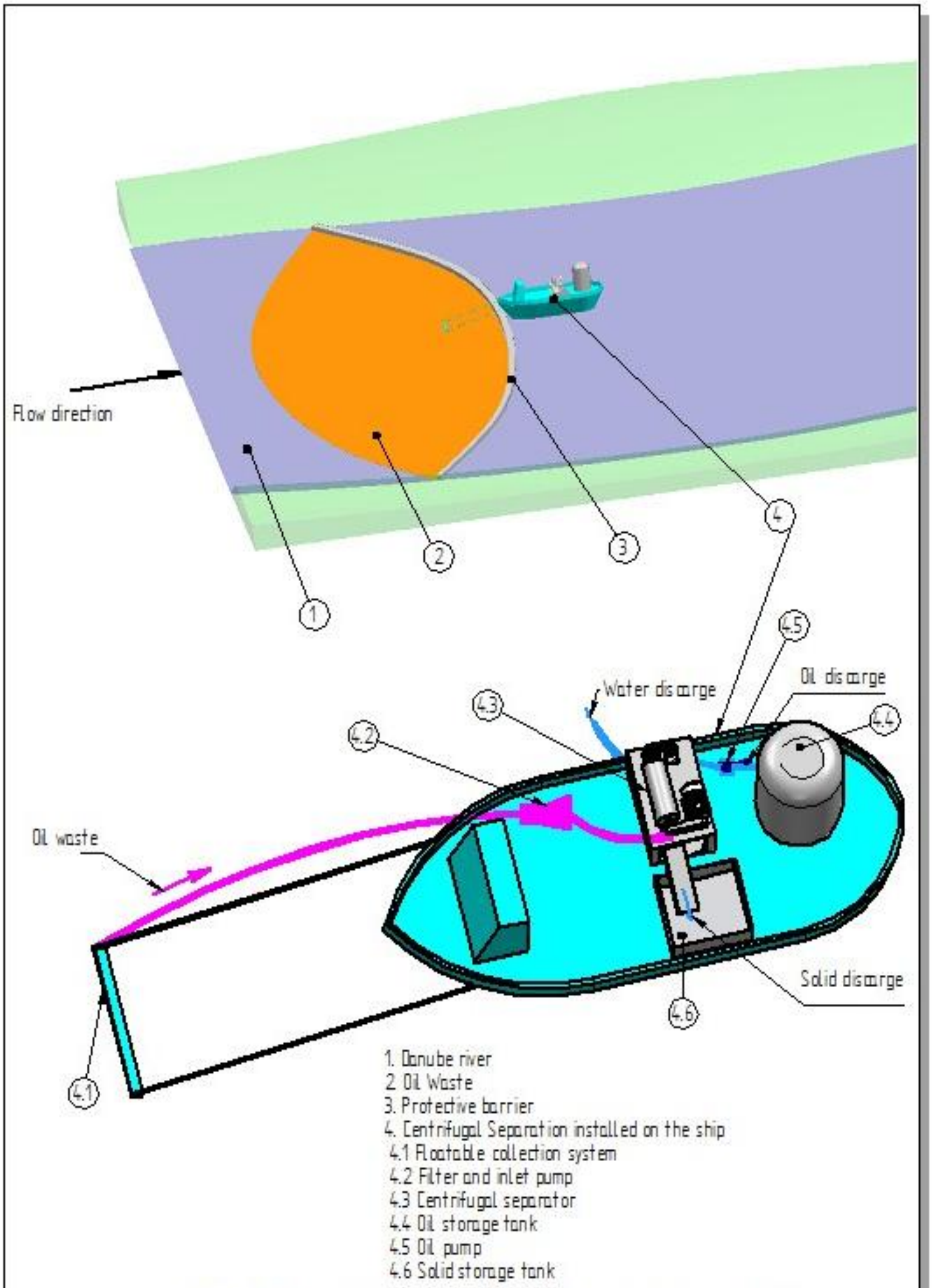
For this reason, on both banks of the Danube, water quality monitoring stations to be able to identify in short-time phenomenon of pollution and prevent its spread. One way to avoid extending the effect of pollution is to install protective barriers which hold pollutants that will subsequently be recovered by the proposed technology.

Respecting the general scheme of **Fig.7**, **study no. 2** for a waste oil separation system in **fig. 5** shows the operational plan for the recovery of pollutants by centrifugal separator plant mounted on a ship.

Fig.6 shows the operational plan for the recovery of polluants by centrifugal separator plant mounted on a ground vehicle.

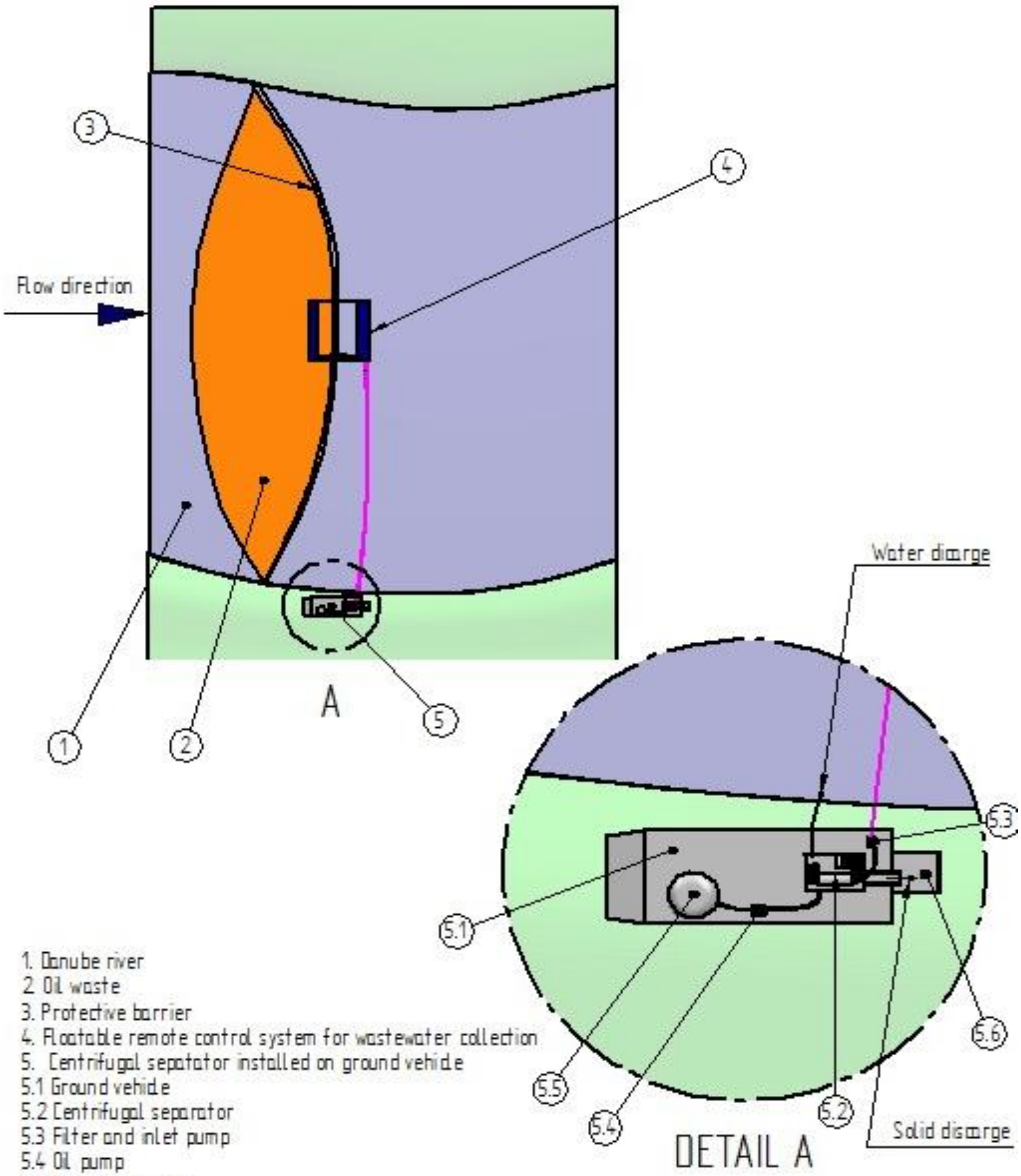
The operational plan for recovery of polluants by centrifugal separator plant mounted fix on ground is the same as the one shown in fig. 6 particularity is that all units are mounted in a fixed ground station.

For all cases presented is necessary that the facility be provided with adequate power sources as follows: 220 single phase, 380 three phase and 24 Vcc for power plant control.



1. Danube river
2. Oil Waste
3. Protective barrier
4. Centrifugal Separation installed on the ship
 4.1 Floatable collection system
 4.2 Filter and inlet pump
 4.3 Centrifugal separator
 4.4 Oil storage tank
 4.5 Oil pump
 4.6 Solid storage tank

Fig. 15 Operational scheme for ship-mounted installation



1. Danube river
2 Oil waste
3. Protective barrier
4. Floatable remote control system for wastewater collection
5. Centrifugal sepatator installed on ground vehicle
5.1 Ground vehicle
5.2 Centrifugal separator
5.3 Filter and inlet pump
5.4 Oil pump
5.5 Oil storage tank
5.6 Solid storage tank

Fig .6 Operational scteme for a ground vehicle-mounted installation
(For a grounded wastewater collection system all equipments will have the same configuration)

3.2 Technological implications

3.2.1 Considerations on the chemical composition and phisical properties of crude oils and petroleum fractions, potentially involved in the Danube river pollution.

Classes of chemical compounds present in crude oil

Hydrocarbons from crude oil are from classes: paraffins, naphthenes, aromatic hydrocarbons with mixed structure, containing up to 100 carbon atoms in the molecule and belong to 17 homologous series, between C_nH_{2n+2} and C_nH_{2n+3}.

Crude oil does not contain unsaturated hydrocarbons (alkenes, alkadienes, alkynes).

Hydrocarbons are the major component of the oil: over 50% in the oils with aromatic naphthenes, and about 90-98% in the wax (paraffin) oils. The number of individual hydrocarbons from crude oil is very high, not known because of its high compositional complexity.

It is estimated that about ca. 500 hydrocarbons are present only in gasoline fraction, with distillation limits of 40-180 ° C.

The number of present hydrocarbons increases equally with the increasing of distillation limits of petroleum fractions, due to the growing of carbon atoms number in the molecule, respectively the number of possible isomers.

However, although the number of hydrocarbons present in crude oil is extremely high, their weight is different, which makes the oils are composed largely of a relatively small number of hydrocarbons.

Thus, for crude oil from Ponca, Oklahoma (U.S.A), approx. 50% of oil is composed of only 150 hydrocarbons from as above mentioned classes, in crude oil are present about the same hydrocarbons, but in varying proportions, leading to differences between the various oils.

The abundance of various hydrocarbons in crude oils is in a wide range, from thousandths and hundredths of a percent to several percents.

The average (200-350 ° C) and higher (over 350 ° C) fractions of crude oil, are found in high proportion hydrocarbons with mixed structure (hydroaromatics).

The relative content of individual neighboring hydrocarbons from a class is approximately constant.

The best studied are hydrocarbons present in the light fractions of petroleum (gas, gasoline, petrol, those who distill up to 200 ° C), being identified most of the individual components.

For middle and higher fractions of crude oil, due to their great compositional complexity, only in a few cases it has succeeded separations and identifications of individual hydrocarbons, the best studied being the linear paraffins (normal) and aromatics.

Paraffinic hydrocarbons present in oils are of the linear (normal-paraffins) and branched (isoparaffins) types, in oil deposit being present both lower terms, components of associated gases, and higher terms, solid and liquid paraffin with up to 80 (100) carbon atoms in the molecule.

The proportion of paraffins in crude oils and its separated fractions widely varies, as function of their chemical nature (waxy or unasked), and distilling range (distillation limits) of the fractions. Young geological age oils (60 - 80 million years) have a lower content of paraffinic hydrocarbons, compared with the old ones (160 - 180 million years), these being more advanced in terms of their chemical transformations, so more rich in paraffins.

In waxy crude oils, normal paraffin hydrocarbons are found in greater proportion than branched ones, in which they may represent cca. 25% from oil. For unasked oil, in some of its separate fractions, the proportion of isoparaffins may exceed the normal paraffins proportion.

Wax content in oil increases with increasing of number of carbon atoms in the molecule, reaching the maximum of 2.5% of crude oil, for n-C8 hydrocarbons, then a gradual decline occurs, so that the proportion of hydrocarbon is only approx. 0.1%.

In various successive fractions separated from oils, paraffin hydrocarbons ratio decreases with the increase of their distillation range: in lower fractions (under 200 ° C) approx. 80%, medium fractions (200-350 ° C) approx. 55-60%, and in the residual oil fractions (over 500 ° C) till 5-20%.

Normal paraffin hydrocarbons from crude oil are the best studied because they can be relatively easily separated by various methods: urea treatment, molecular sieve separation, various chromatographic techniques. Linear paraffin components were separated and identified from all oil fractions: gas, gasoline, distillate oil, diesel fuel, oils.

Branched paraffinic hydrocarbons (isoparaffins) are in higher proportion in un waxed oils (naphthenes - aromatic), many of its components being in a so low proportion that they can not be separated and identified. In average fractions of the oil, paraffinic branched hydrocarbons with isoprenoide structure have been identified, these being probably from the organic material from which oil was formed. In the oils and their fractions there are isoparaffins with few branches: one to three branches per molecule, isoparaffins with one branch being more abundant than those with two branches, which in turn are found in greater proportion than those with three branches

For isoparaffins with one branch, the components with the branch placed at the second carbon atom of the main chain are in greater proportion than those with the branch placed in the third carbon atom, etc.. The most frequently branches are methyl and ethyl groups.

The most components have methyl group branch linked at positions 2 and 3 of the main chain.

Naphthenic hydrocarbons are the main components of the most oils, whatever their chemical nature, the content of these hydrocarbons varying between 30-50%.

As chemical structure, they are alkylcyclopentans, alkylcyclohexans and polycyclic types, with up to ten cycles per molecule

The most abundant are metilcyclohexan (the most abundant naphthenic component of crude oil), followed by metilcyclopentan. The lower oil fractions contain cyclopentane derivatives in a greater proportion than cyclohexane derivates, while in the upper fractions, the cyclohexane derivates are in a significantly higher proportion.

At the same number of carbon atoms in the molecule, the alkylnaftens with three side chains are in a significantly higher proportion. The alkylnaftens with two substituents on the same carbon atom of the cycle are in a very low proportion in oil.

Most of the mono-naphthenes from the crude oil are mono and dicyclic.

The physical characteristics of naphthenes have intermediate values between those of paraffins and aromatics. The differences are more pronounced for lower terms, being lower with the length of side chains increasing.

It must be mentioned that the melting temperature of cyclohexane is high (+6.4 ° C) compared with other components.

It must be also highlighted the fact that monocyclic alkylnaftenes with over than 15 carbon atoms in the linear chain are solid at room temperature, such structures being components of petroleum waxes. For polycyclic naphthenes, the physical characteristics values are higher, much higher as cyclization degree is more advanced.

Regarding solubility, the naphthenes are more soluble than paraffins in various solvents, being mentioned that at alkylnaphthenes, if the side chain length increase and at polycyclic naphthenes the solubility increases if the cyclization range decreases.

Being saturated hydrocarbons, the naphthenes have a high chemical stability, similar to that of alkanes. Among the many reactions of naphthenes that give interest to our discipline are those with sulfuric acid of 98% concentration, naphthenes non reacting with it at low temperature conditions, and catalytic dehydrogenation reaction of cyclohexane with formation of alkylbenzenes, major reaction in reforming catalytic process, as analytically, because it allows the dosage of the hydrocarbons from non-aromatic gasoline (Zelinski method)

The number of carbon atoms from the side chains attached to naphthenic cycle's increases with increasing of average boiling temperature of successive fractions separated from oils, for a given degree of cyclization, and decreases with the increasing of cycles number per molecule, as seen from the data presented Table 3

Table 3 Naphthenic hydrocarbons present in high successive fractions separated from Webster crude oil

	Hidrocarbons, % weight, in fraction(°C)		
Hidrocarbons class	315-370	370 - 426	426 - 482
Total naphthenes	72,5	67,5	69,0
Monocyclic naphthenes	31,5	17,5	7,0
Dicyclic naphthenes	30,5	30,0	19,0
Tricyclic naphthenes	9,5	15,5	25,5
Tetracyclic naphthenes	1,0	5,0	8,5
Pentacyclic naphthenes		1,5	7,0
Hexacyclic naphthenes			2,0

Table.4. Number of carbon atoms in the side chains of naphthenic hydrocarbons

Alkilnaphthenes	Number of carbon atoms in the side chains of naphthenic hydrocarbons, fraction components (°C):		
	315-370	370-426	426 - 482
Monocyclic	14	20	28
Dicyclic	9	15	23
Tricyclic	6	12	20
Tetracyclic	3	9	17
Pentacyclic	-	5	13
Hexacyclic	-	9	9

The polycyclic naphthenic hydrocarbons contain more side chains, but shorter. In finished lubricating oils (commercial) is unlikely to exist linear chain longer than 15 carbon atoms, because such hydrocarbons have a high melting point and are removed by de waxing process.

Aromatic hydrocarbons are the third main component of hydrocarbons present in crude oil; the proportion of such hydrocarbons is less than that of paraffins and naphthenes, separately taken, and varies depending on the chemical nature of the oil, waxy (wax) or unasked (naphthenes, aromatic), between 10-50%.

In successive fractions separated from crude oil aromatic proportion increases with the average temperature of boiling, so that the upper fractions of aromatic oil proportion can exceed that of paraffin

Aromatic hydrocarbons with different structure are present in crude oil, with one to ten cycles per molecule, the highest proportion of aromatics in all fractions of crude oil beeng represented by alkylbenzenes with a varied numbers of side chains, of different lengths.

Polycyclic aromatic hydrocarbons are mostly of condensed type, less substituted

The values of physical characteristics (boiling point, density, refractive index) are in the most cases higher than those presented by paraffinic and naphthenic components, with the same number of carbon atoms in molecule

Lower alkylbenzenes, with one to three short alkyl substituents, are liquid at room temperature, except β-xylene (tt = + 13.3 ° C); also benzene has relatively high melting temperature (5.5 ° C); highly substituted alkylbenzenes are solid (eg, tetramethyl benzene, tt = 79).

The nonsubstituted polycyclic aromatic hydrocarbons, and some of their alkyl derivatives have high melting temperature, being solid; there are obvious differences between saturated and aromatic hydrocarbons, at the same number of carbon atoms in the molecule, in terms of density and refractive index values, two of the most commonly characteristics, analytical used.

In terms of solubility in various solvents, the aromatic hydrocarbons are different than the saturated (para-naphthenic): the inferior aromatic hydrocarbons are totally soluble in organic solvents such as alcohols, ethyl ether, acetone, hydrocarbons; the main characteristic for all aromatic hydrocarbons with short chain is their high solubility in selective solvents, such as phenol, furfural, aniline, etc., specific behavior which is actually used for the separation of such components from other classes of hydrocarbons, in extraction process, at both analytical and industrial level.

The aromatic hydrocarbons are involved in conducting of many chemical reactions, in particular the substitution; of particular importance are: the reaction with sulfuric acid, because it allows the separation and determination of aromatic hydrocarbon from small petroleum fractions by atmospheric distillation (sulphurimetric method), the reaction with picric acid (trinitrophenol), useful for separating aromatics (mono-and diciclice) from their mixture with other hydrocarbons and formolit reaction between aromatic hydrocarbons and formaldehyde in the presence of sulfuric acid, a reaction used to highlight the presence of aromatics in a petroleum product

Mononuclear aromatic hydrocarbons are present in the lower fractions of oil: benzene, toluene, xylene, ethyl benzene, n-and iso-propilbenzen, the most abundant being toluene, ethyl benzene and m-xylene

In the literature is mentioned the presence of indene and its derivatives, aromatic dicyclic hydrocarbons in the fractions separated from the Oklahoma Ponca crude oil; the alkylbezenes proportion in petrol is higher than that of benzene; alkylbenzenes content decreases with increasing of carbon atoms number in the side chain, while the proportion of alkylbenzenes with the same number of carbon atoms per molecule increases with side chain increasing; in the lower fractions of crude oil were not identified alkylbenzenes with one normal chain, more than 4 carbon atoms

The aromatic hydrocarbon content of petrol is lower than that of paraffins, respectively naphthenes, being of 10-30%, depending on the origin and nature of petroleum and fraction distillation interval.

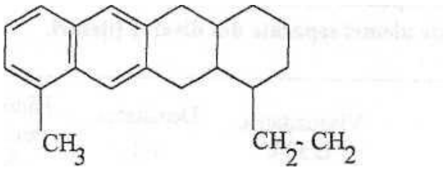
The increasing of the aromatic hydrocarbons proportion with the growing of the range of distillation of successive petroleum fractions, conducts to a relatively high content of aromatic hydrocarbons in fractions separated from Romanian oils. Aromatic hydrocarbons content of gasoline integral fraction, separated from different crude oils is between 7-19% weight.

A high proportion of aromatic hydrocarbons in gasoline is desirable, given their higher octane and giving the best combustion properties of gasoline in spark ignition engines (toluene is 104 octane, benzene 99, IPB, 99.3, etc.).

At higher fractions of oil there are more frequently aromatics like alkylbenzenes type with one or two chains, one of which being short (methyl), the other longer and branched and polycyclic aromatics with 2 to ten cycles per molecule, most frequently condensed; the polycyclic nature of aromatic components increases with increasing the average temperature of boiling of successive fractions separated from crude oil.

Among polycyclic aromatics, are frequently found the alkyl naphthalene and its alkyl derivatives; from tricyclic derivatives, those of phenanthrene are found in higher proportion than those of anthracene. The presence of aromatic hydrocarbon in oil fractions, especially polycyclic ones, is undesirable because they have low viscosity indices, high density, high viscosity and high coke numbers, in which case they are removed, for the most part, particularly polycyclics, by selective solvent extraction.

Hydrocarbons with mixed structure (hydroaromatics) appear in distilled petroleum fractions at above 200 ° C. In their composition, in addition to those mentioned classes of hydrocarbons (paraffins, naphthenes, aromatics) are, with the percentage increasing as it grows the distillation range (average boiling temperature) of the fraction, hydrocarbons with mixed structure (hydroaromatics) whose molecule contains, in various proportions, the three structural elements: cycles aromatic condensed with naphthenic rings, with paraffinic chains attached to them, usually attached to the naphthenic cycles, on the aromatics ones being grafted short chains (methyl): - CH_2-CH



The proportion of these structures is high in residual and heavy fractions of crude oil, according to some authors, these fractions are exclusively composed of such components. Naphthenic and aromatic rings are condensed type; paraffin chains are short, the number of carbon atoms being of around ten.

Chemical compositions and physical diversity of the estate of petroleum products, which may be potential pollutants, needs to remove their effects and design effective technology adaptable to specific conditions.

For this reason, using a mobile laboratory to determine in a short time the physical and chemical properties of pollutants and based on their schedule to the optimum functional parameters of the centrifuge plant. These parameters will be determined both by calculation and by simulating the process of separation using CFD (Computational fluid dynamics).

3.2.2 General considerations on the chemical and physical properties of surface water as input data for constructional versions

3.2.2.1 Total petroleum hidrocarbons (TPH)

The toxicity of petroleum and petroleum products may be immediate or long term.

The immediate toxicity is caused by:

- high concentrations of saturated hydrocarbons, which can cause organisms death, especially the young forms;
- olefinic hydrocarbons, which have an intermediate toxicity between the saturated and the aromatic oners;
- aromatic hydrocarbons, which are the most toxic.

Long-term toxicity leads to ecological imbalances, due to changes in soil fractions in the water, which in low concentrations interferes with several chemical messengers, involved in nutrition and reproduction of many aquatic organisms

Oil reached water suffers transformations, and pellicle formation on the surface lead to effects such as:

- Lowering of the light amount that penetrates the water, leading to decreasing of the plants photosynthesis intensity (Fig. 7)

Fig. 7

- Oxygen decreasing in the water, with the effect of destroying aquatic flora and fish death (Fig.8);

Fig. 8

- Evaporation of volatile products from petroleum film, reaching the atmosphere (Fig. 9)

Fig. 9

- Gradual sedimentation of heavier fractions;
- Due to wind action, the oil film is carried to shore, invading beaches, coastal areas, the areas washed by the tide - an area rich in flora and fauna (Fig. 10, 11)

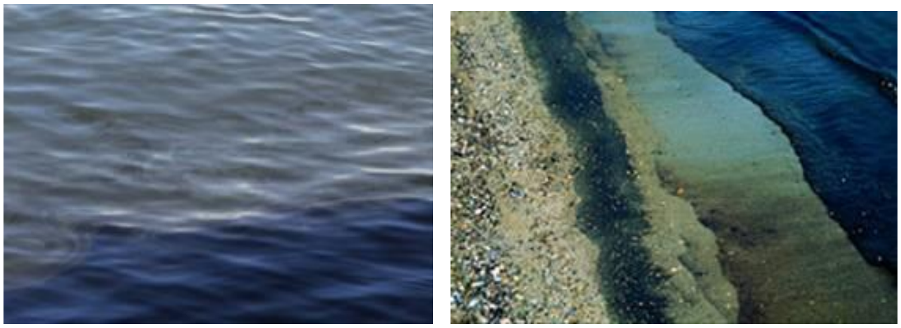


Fig. 10

Fig. 11

Petroleum hydrocarbons (PHCs) are common contaminants, but, paradoxical, they are not generally regulated as hazardous wastes. Methods for sampling and analysis of environmental media for the family of PHCs are generally thought of as TPH methods.

The acronym PHC (petroleum hydrocarbons) is widely used to refer to the hydrogen- and carbon-containing compounds originating from crude oil, but it should be distinguished from TPH, because TPH is specifically associated with environmental sampling and analytical results. Petroleum products are complex mixtures of hundreds of hydrocarbon compounds, ranging from light ,volatile, short-chained organic compounds to heavy, long-chained, branched compounds. The exact composition of petroleum products varies depending upon the source of the crude oil and the refining practices used to produce the product.

During the refining process, crude oil is separated into fractions having similar boiling points. These fractions are then modified by cracking, condensation, polymerization, and alkylation processes, and are formulated into commercial products such as naphtha, gasoline, jet fuel, and fuel oils. The composition of any one of these products can vary based on the refinery involved, time of year, variation in additives or modifiers, and other factors. The chemical composition of the product can be further affected by weathering and/or biological modification upon release to the environment, water in our case.

The chemical composition of petroleum products is complex and may change over time following release into the environment. These factors make it difficult to select the most appropriate analytical methods for evaluating environmental samples.

Hydrocarbons in water can be found as free floating, emulsified, dissolved, or adsorbed to suspended solids.

TPH is sometimes referred to as mineral oil, hydrocarbon oil, extractable hydrocarbon, oil or grease. There are many analytical techniques available that measure TPH concentrations in the environment. No single method measures the entire range of petroleum-derived hydrocarbons .Because the techniques vary in the way hydrocarbons are extracted, cleaned up, and detected, they each measure slightly different subsets of the petroleum-derived hydrocarbons present in a sample.

The same sample analyzed by different methods may produce different TPH values. For this reason, it is important to know exactly how each determination is made. Interpretation of the results depends on understanding the capabilities and limitations of the selected method.

Microbes in the soils and water have a natural ability to breakdown many of the these compounds and any hydrocarbon which is exposed to the air will also have an affinity to volatilize. As well, reactions including photochemistry and the various transformations of the hydrocarbon through these reactions can enhance the hydrocarbon decomposition.

Industrial processes and man induced activities often result in the increased loading of hydrocarbons in water.

Understanding hydrocarbons and the techniques to monitor for them is an important part in the assessment of filters and separators, and the associated productivity and environmental impacts they can have.

There can be many confusing references to hydrocarbon contamination water. Terminology such as PAH's (polycyclic aromatic hydrocarbons), BTEX (benzene, ethylbenzene, toluene, xylene), TPH (total petroleum hydrocarbons), TRPH (total recoverable petroleum hydrocarbons), TOG (total oil and grease) Organic vs. Inorganic,…all contribute to this confusion.

Generally, hydrocarbon contamination in water is directed to total parts per million (ppm) levels of the hydrocarbon in water. For example, a hydrocarbon level of 30 ppm in water could contain any number of compounds that total this 30 ppm; including compounds found in jet fuels, diesels, lubricating oils, etc.. In other words, the source of the hydrocarbon and the specific compound is not particularly targeted. It is the overall total of hydrocarbon compounds that is typically of interest.

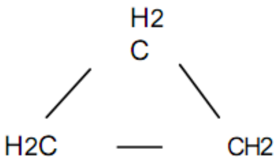
A hydrocarbon, by definition, is one of a group of chemical compounds composed only of hydrogen and carbon. Typically, hydrocarbons are broken down into three main classes; aliphatic, alicyclic, and aromatics.

Aliphatics are open chain compounds, bonded in a linear fashion, and are saturated or unsaturated. Saturated (single bond) aliphatics are often referred to as paraffins or alkanes. Unsaturated aliphatics are known as olefins or alkenes (double bond), acetylenes or alkynes (triple bonds), diolefins or alkadienes (two double bonds), and alkatrienes and alkeynes (multiple double or triple bonds). Typical aliphatics include ethane, acetylene, and 1,2-butadiene, and the most popular, methane.

$$CH \equiv CH$$

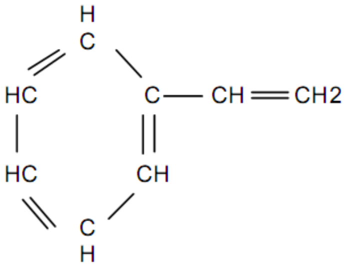
Aliphatic triple bond compound example: acetylene.

Alicyclics, as indicated by their name, contain rings of carbon atoms in their structure. The ring size and number can vary which increases the number and classes of this compound. Multiple ring compounds are referred to as polycyclic alicyclic compounds. The saturated alicyclic hydrocarbons are often called napthalenes. Examples of alicyclics include cyclopropane and cyclopentane.



Alicyclic compound example: cyclopropane

Aromatics typically contain at least one 6-membered benzene ring in their make-up. Polycyclic aromatic hydrocarbons (PAHs) therefore include multiple ring compounds that include the benzine ring. A few aromatic compounds include ethylbenzine, vinylbenzine (styrene), toluene, xylene. The aromatics include what are often referred to as BTEX compounds.



Aromatic compound example: vinylbenzene (styrene)

Most unrefined crude oil does not contain high concentrations of aromatic hydrocarbons. The aromatic hydrocarbons are typically the result of the refining process and are produced during the distillation (cracking) operations of a facility. Aromatics are therefore commonly associated with gasoline, jet fuels, diesel, kerosene, lubricating oils, and transformer oils.

As such, the aromatics are typically the target of monitoring instruments to verify distillation efficiency, filtration and separation effectiveness, and environmental contamination.

Generally, measurement techniques can be categorized as discrete sample or continuous on-line devices. Typical approaches to monitoring include: gravimetric (weight), colorimetric, infrared, UV absorption, nephelometry, or fluorescence.

While the definition of an hydrocarbon may be quite clear, the definition of a hydrocarbon contamination in water is not as clear. The type of hydrocarbon and the ability to reliably monitor for it within practical means plays an important role in this definition.

3.2.2.2. Total solids

By definition, the amount of suspended sediment for 2 hours is called sediment.

The term "total solids" refers to matter suspended or dissolved in water or wastewater, and is related to both specific conductance and turbidity (Fig. 12). Total solids (also referred to as **total residue**) are the term used for material left in a container after evaporation and drying of a water sample. **Total Solids** includes both **total suspended solids**, the portion of total solids retained by a filter and **total dissolved solids**, the portion that passes through a filter (American Public Health Association, 1998).

Total solids can be measured by evaporating a water sample in a weighed dish, and then drying the residue in an oven at 103 to 105° C. Instead of total solids, laboratories often measure total suspended solids and/or total dissolved solids.

Fig. 12

Total Suspended Solids (TSS)

Total Suspended Solids (TSS) are solids in water that can be trapped by a filter. TSS can include a wide variety of material, such as silt, decaying plant and animal matter, industrial wastes, and sewage. High concentrations of suspended solids can cause many problems for stream health and aquatic life.

As TPH, high TSS can block light from reaching submerged vegetation. As the amount of light passing through the water is reduced, photosynthesis slows down. Reduced rates of photosynthesis causes less dissolved oxygen to be released into the water by plants. If light is completely blocked, the plants will stop producing oxygen and will die. As the plants are decomposed, bacteria will use up even more oxygen from the water. Low dissolved oxygen can lead to fish kills. High TSS can also cause an increase in surface water temperature, because the suspended particles absorb heat from sunlight. This can cause dissolved oxygen levels to fall even further (because warmer waters can hold less DO), and can harm aquatic life in many other ways.

The decrease in water clarity caused by TSS can affect the ability of fish to see and catch food. Suspended sediment can also clog fish gills, reduce growth rates, decrease resistance to disease, and prevent egg and larval development. When suspended solids settle to the bottom of a water body, they can smother the eggs of fish and aquatic insects, as well as suffocate newly hatched insect larvae. Settling sediments can fill in spaces between rocks which could have been used by aquatic organisms for homes.

High TSS in a water body can often mean higher concentrations of bacteria, nutrients, pesticides, and metals in the water. These pollutants may attach to sediment particles on the land and be carried into water bodies with storm water. In the water, the pollutants may be released from the sediment or travel farther downstream

Also, high TSS can cause problems for industrial use, because the solids may clog or scour pipes and machinery.

The importance of fluvial sediment to the quality of aquatic and riparian systems is well established. The main two methods for determining the total amount of suspended material in a water sample are: “Determining Sediment Concentration (SSC) in water samples” and “Total Suspended Solids dried (TSS) at 103–105°C”.

The fundamental difference between the SSC and TSS analytical methods stems from preparation of the sample for subsequent filtering, drying, and weighing. A TSS analysis normally entails withdrawal of an aliquot of the original sample for subsequent analysis. The SSC analytical method measures all sediment and the mass of the entire water-sediment mixture. Additionally, the percentage of sand-size and finer material can be determined as part of the SSC method, but not as part of the TSS method.

Factors Affecting Total Suspended Solids are:

- High Flow Rates
- Soil Erosion

- Wastewater and Septic System Effluent
- Decaying Plants and Animals
- Bottom-Feeding Fish

As organic and mineral particles that are transported in the water, TSS is closely linked to land erosion and to erosion of river channels. TSS can be extremely variable, ranging from less than 5 mg L^{-1} to extremes of 30,000 mg L^{-1} in some rivers. TSS is not only an important measure of erosion in river basins, it is also closely linked to the transport through river systems of nutrients (especially phosphorus), metals, and a wide range of industrial and agricultural chemicals.

In most rivers TSS is primarily composed of small mineral particles. TSS is often referred to as turbidity and is frequently poorly measured. Higher TSS (>1000 mg L^{-1} may greatly affect water use by limiting light penetration and can limit reservoir life through sedimentation of suspended matter. TSS-levels and fluctuations influence aquatic life, from phytoplankton to fish. TSS, especially when the individual particles are small (< 63µm), carry many substances that are harmful or toxic. As a result, suspended particles are often the primary carrier of these pollutants to lakes and to coastal zones of oceans where they settle. In rivers, lakes and coastal zones these fine particles are a food source for filter feeders which are part of the food chain, leading to biomagnification of chemical pollutants in fish and, ultimately, in man. In deep lakes, however, deposition of fine particles effectively removes pollutants from the overlying water by burying them in the bottom sediments of the lake. In river basins where erosion is a serious problem, suspended solids can blanket the river bed, thereby destroying fish habitat.

Time series of instantaneous TSS loads (kg s^{-1}) provides useful information about the physical behaviour of rivers. Because total suspended solids concentration is partly a function of discharge, TSS load increases as discharge increases. In many rivers, the amount of sediment (solids) in transport (the load) can vary over three or more orders of magnitude during the year.

Total Dissolved Solids (TDS)

Total dissolved solids (TDS) concentrations are generally inversely proportional to river discharge (Q). This relationship is the result of the mixing of more mineralized groundwaters that dominate during baseflow, with more dilute surface runoff waters. This can been seen when seasonal TDS variation is plotted with corresponding discharges. Relative variations can be quite high: from 30% for rivers with low TDS levels to 200% or even 400% for more saline rivers (Fig. 13). TDS can rise proportionately with flow (Q) in arid regions where leaching of salt deposits can occur during the rising stage of the flood.

Fig. 13

*3.2.2.*3. Turbidity

Fig. 14

Water turbidity is given by very fine particles in suspension, which do not deposit over time. A troubled waters presents an epidemiological threat, because the particles in suspension may be a nutrient medium for bacteria.

Determination of turbidity can be qualitatively, quantitatively and semi quantitatively performed.

Turbidity is the amount of cloudiness in the water . This can vary from a river full of mud and silt where it would be impossible to see through the water (high turbidity), to a spring water which appears to be completely clear (low turbidity). Turbidity can be caused by :

- silt, sand and mud ;
- bacteria and other germs ;
- chemical precipitates.

It is very important to measure the water turbidity

Turbidity can be measured using either an electronic turbidity meter or a turbidity tube.

Both methods have advantages and disadvantages, as shown below. Turbidity is usually measured in nephelometric turbidity units (NTU) or Jackson turbidity units (JTLJ), depending on the method used for measurement. The two units are roughly equal.

The major source of turbidity in the open water zone is typically phytoplankton , but closer to shore, particulates may also be clays and silts from shoreline erosion, resuspended bottom sediments (this is what turns the western arm of Lake Superior near Duluth brown on a windy day), and organic detritus from stream and/or wastewater discharges. Dredging operations, channelization, increased flow rates , floods, or even too many bottom-feeding fish (such as carp) may stir up bottom sediments and increase the cloudiness of the water.

High concentrations of particulate matter can modify light penetration, cause shallow lakes and bays to fill in faster, and smother benthic habitats - impacting both organisms and eggs. As particles of silt, clay, and other organic materials settle to the bottom, they can suffocate newly hatched larvae and fill in spaces between rocks which could have been used by aquatic organisms as habitat. Fine particulate material also can clog or damage sensitive gill structures, decrease their resistance to disease, prevent proper egg and larval development, and potentially interfere with feeding activities. If light penetration is reduced significantly, macrophyte growth may be decreased which would in turn impact the organisms dependent upon them for food and cover. Reduced photosynthesis can also result in a lower daytime release of oxygen into the water. Effects on phytoplankton growth are complex depending on too many factors to generalize.

Romania and Bulgaria are two important countries in the Danube Basin, both from the surface and population point of view, and, therefore, have a significant impact on the river

Moreover, the Danube discharges its waters into the Black Sea through the Danube Delta which is largely located in Romania.

The ecosystems of the Danube River Basin are highly valuable in environmental terms and support a large number of economic and social activities. Therefore, on 29 June 1994, the Convention on Cooperation for the Protection and Sustainable Use of the River Danube (Danube River Protection Convention) was signed in Sofia.

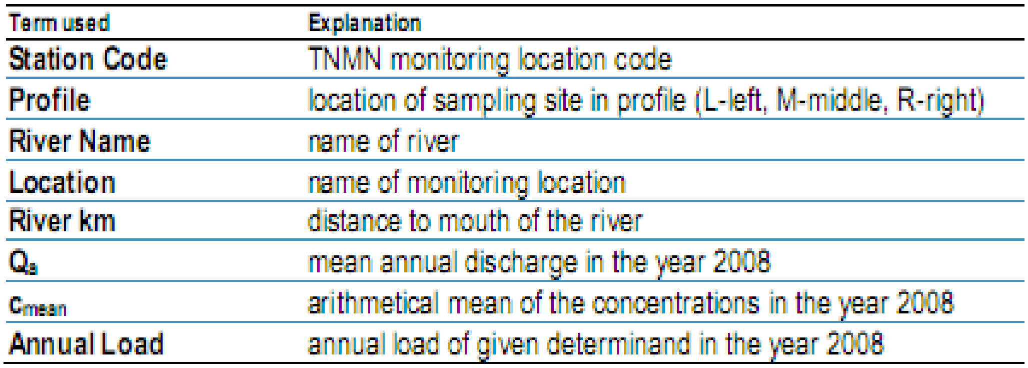
Since 2000, the ICPDR has also been the coordinating body for implementing the EU Water Framework Directive (WFD) — the legal mechanism for managing water in the European Union.

During more than 15 years of existence, the ICPDR has established a number of products and tools which support joint activities and sustainable development.

One of the most important early achievements was the Transnational Monitoring Network (TNMN), managed by the ICPDR on the basis of national monitoring stations. This provides information on the ecological and chemical status of Danube basin waters.

According to the final version (11.Nov. 2010) of TNMN Annual Report 2008, regarding the water quality in the Danube River Basin, the mean annual concentrations and annual loads of suspended solids, inorganic nitrogen, ortho-phosphate-phosphorus, total phosphorus, BOD5, chlorides and – where available – dissolved phosphorus and silicates - are presented bellow (Tabel 5):

Tabel 5



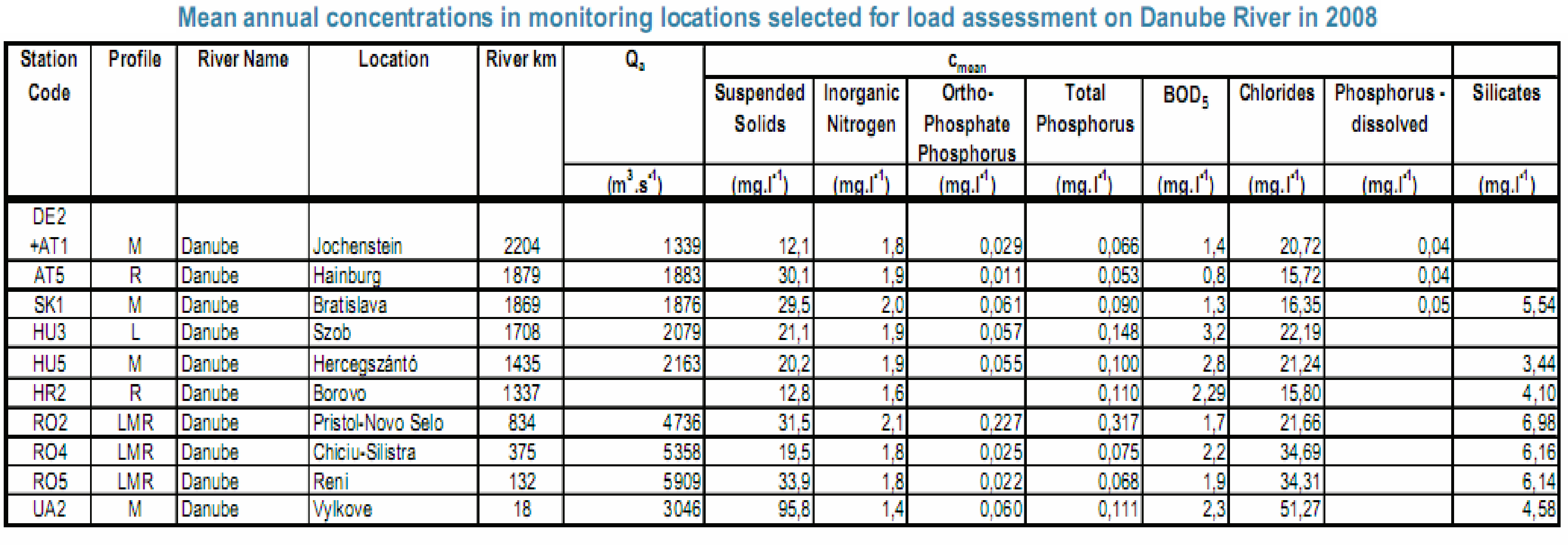
Term used	Explanation
Station Code	TNMN monitoring location code
Profile	location of sampling site in profile (L-left, M-middle, R-right)
River Name	name of river
Location	name of monitoring location
River km	distance to mouth of the river
Q_a	mean annual discharge in the year 2008
c_{mean}	arithmetical mean of the concentrations in the year 2008
Annual Load	annual load of given determinand in the year 2008

To cover pressures of basin-wide importance as organic pollution, nutrient pollution and general degradation of the river, following biological quality elements have been agreed for monitoring:

- Phytoplankton (chlorophyll-a)
- Benthic invertebrates (mandatory parameters: Saprobic index and number of families once yearly, both Pantle&Buck and Zelinka&Marvan SI are acceptable; optional parameters: ASPT and EPT taxa)
- Phytobenthos (benthic diatoms – an optional parameter)

Fig. 15 TNMN Stations along the Danube river

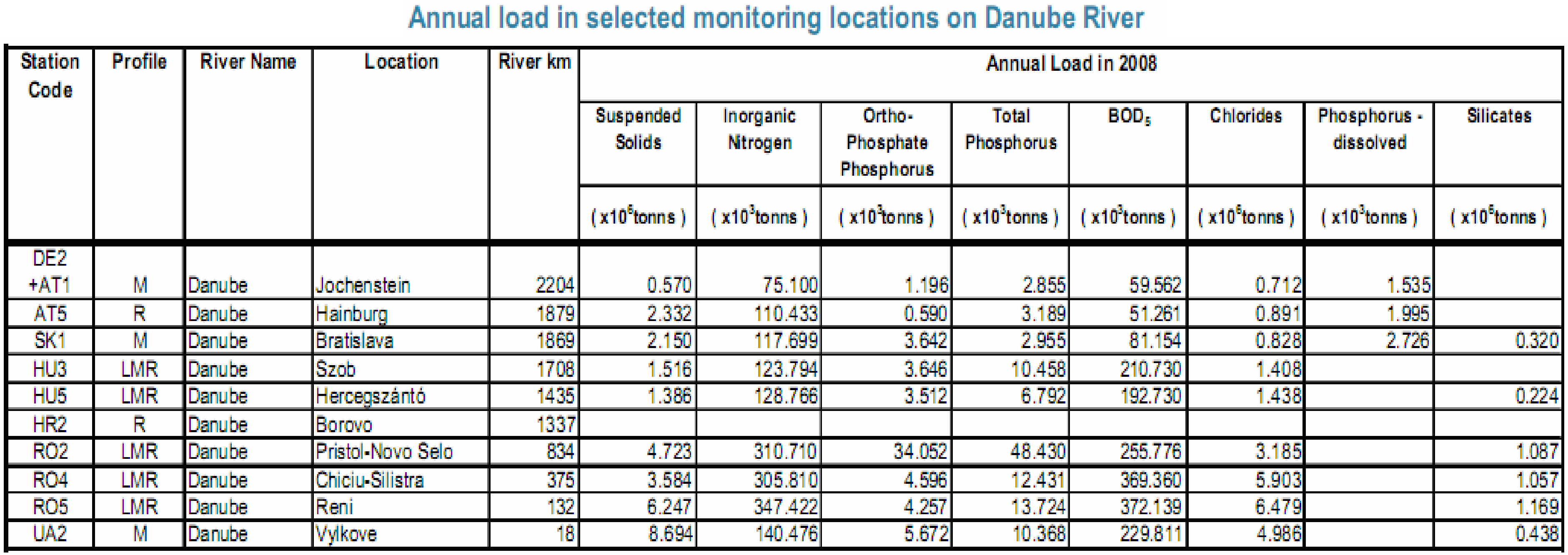
Tabel 6



Mean annual concentrations in monitoring locations selected for load assessment on Danube River in 2008

Station Code	Profile	River Name	Location	River km	Q_a	c_{mean}							
						Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved	Silicates
					$(m^3.s^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$
DE2 +AT1	M	Danube	Jochenstein	2204	1339	12,1	1,8	0,029	0,066	1,4	20,72	0,04	
AT5	R	Danube	Hainburg	1879	1883	30,1	1,9	0,011	0,053	0,8	15,72	0,04	
SK1	M	Danube	Bratislava	1869	1876	29,5	2,0	0,061	0,090	1,3	16,35	0,05	5,54
HU3	L	Danube	Szob	1708	2079	21,1	1,9	0,057	0,148	3,2	22,19		
HU5	M	Danube	Hercegszántó	1435	2163	20,2	1,9	0,055	0,100	2,8	21,24		3,44
HR2	R	Danube	Borovo	1337		12,8	1,6		0,110	2,29	15,80		4,10
RO2	LMR	Danube	Pristol-Novo Selo	834	4736	31,5	2,1	0,227	0,317	1,7	21,66		6,98
RO4	LMR	Danube	Chiciu-Silistra	375	5358	19,5	1,8	0,025	0,075	2,2	34,69		6,16
RO5	LMR	Danube	Reni	132	5909	33,9	1,8	0,022	0,068	1,9	34,31		6,14
UA2	M	Danube	Vylkove	18	3046	95,8	1,4	0,060	0,111	2,3	51,27		4,58

Tabel 7



Annual load in selected monitoring locations on Danube River

Station Code	Profile	River Name	Location	River km	Annual Load in 2008							
					Suspended Solids	Inorganic Nitrogen	Ortho-Phosphate Phosphorus	Total Phosphorus	BOD_5	Chlorides	Phosphorus - dissolved	Silicates
					($x10^6$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^3$tonns)	($x10^6$tonns)	($x10^3$tonns)	($x10^6$tonns)
DE2 +AT1	M	Danube	Jochenstein	2204	0.570	75.100	1.196	2.855	59.562	0.712	1.535	
AT5	R	Danube	Hainburg	1879	2.332	110.433	0.590	3.189	51.261	0.891	1.995	
SK1	M	Danube	Bratislava	1869	2.150	117.699	3.642	2.955	81.154	0.828	2.726	0.320
HU3	LMR	Danube	Szob	1708	1.516	123.794	3.646	10.458	210.730	1.408		
HU5	LMR	Danube	Hercegszántó	1435	1.386	128.766	3.512	6.792	192.730	1.438		0.224
HR2	R	Danube	Borovo	1337								
RO2	LMR	Danube	Pristol-Novo Selo	834	4.723	310.710	34.052	48.430	255.776	3.185		1.087
RO4	LMR	Danube	Chiciu-Silistra	375	3.584	305.810	4.596	12.431	369.360	5.903		1.057
RO5	LMR	Danube	Reni	132	6.247	347.422	4.257	13.724	372.139	6.479		1.169
UA2	M	Danube	Vylkove	18	8.694	140.476	5.672	10.368	229.811	4.986		0.438

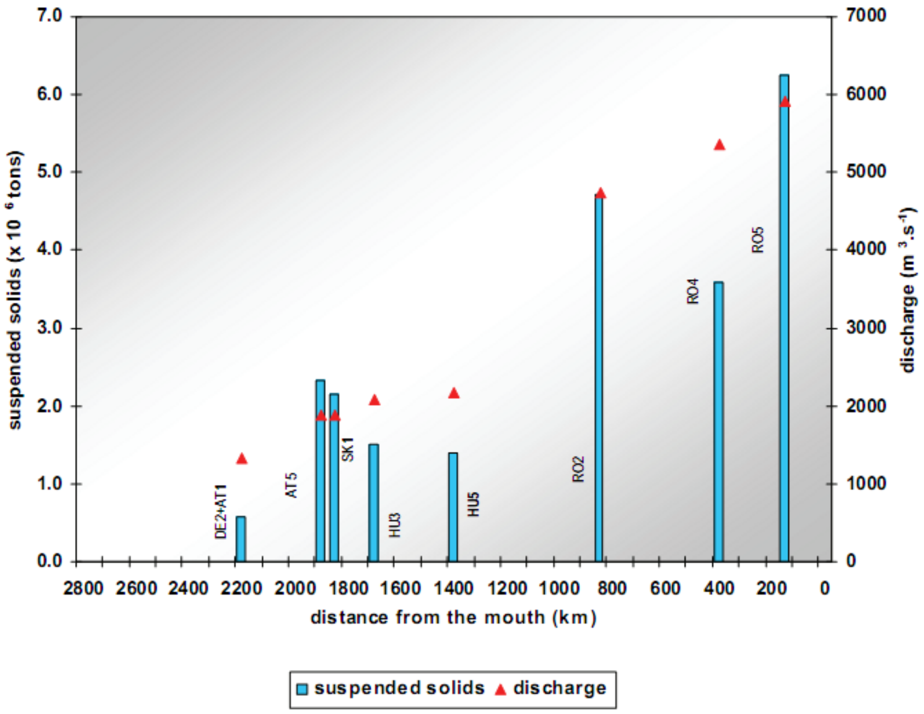


Fig. 16 Annual load of suspended solids
at monitoring locations along the Danube River

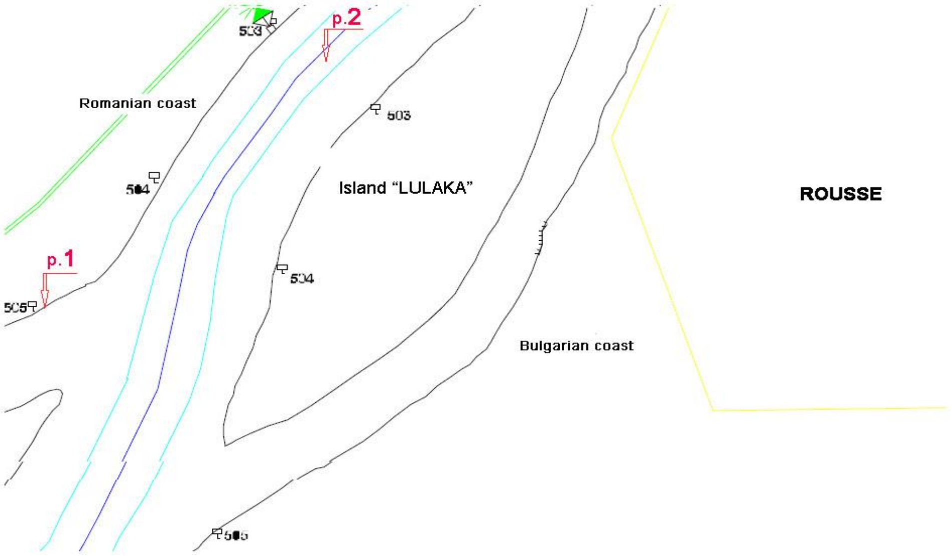
3.2.3. Testing the Danube river

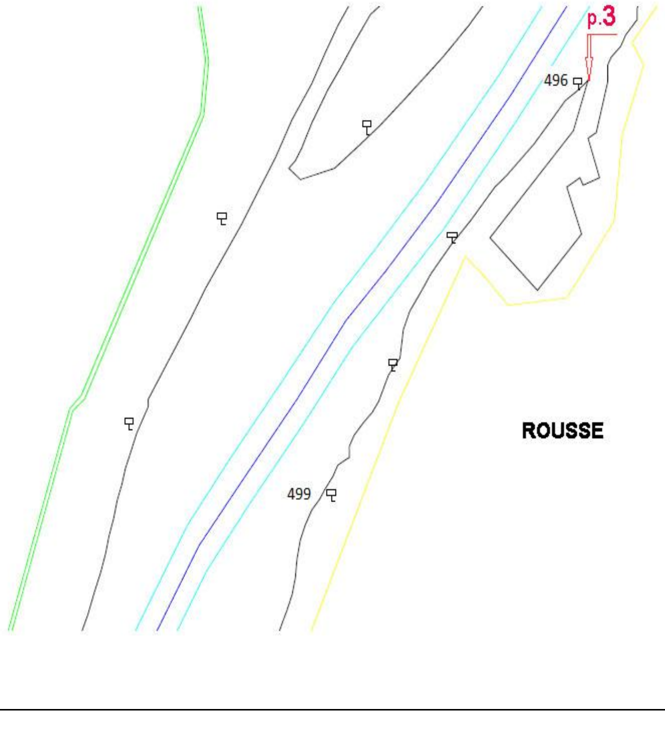
In order to create a common structure for checking and managing Danube pollution, in the frame of this project, Romanian and Bulgarian specialists and researchers have began to perform tests for evaluating the quality of Danube water.These joint technical efforts will help in protecting the environment and to find efficient solutions for cleaning the oil products from polluted water.

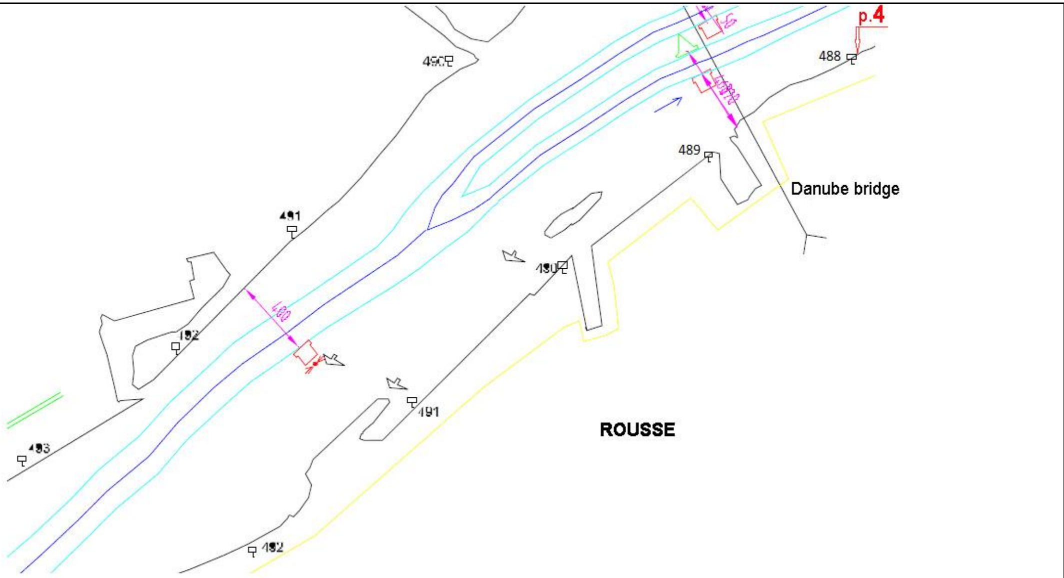
The first tests have been performed by Bulgarian specialists, in 10 locations along the Danube river, Bulgarian coast regions Ruse (6 locations – Fig. 17) and Silistra (4 locations – Fig. 18):

DANUBE RIVER - ROUSSE AREA

(505 кm - 484 кm)







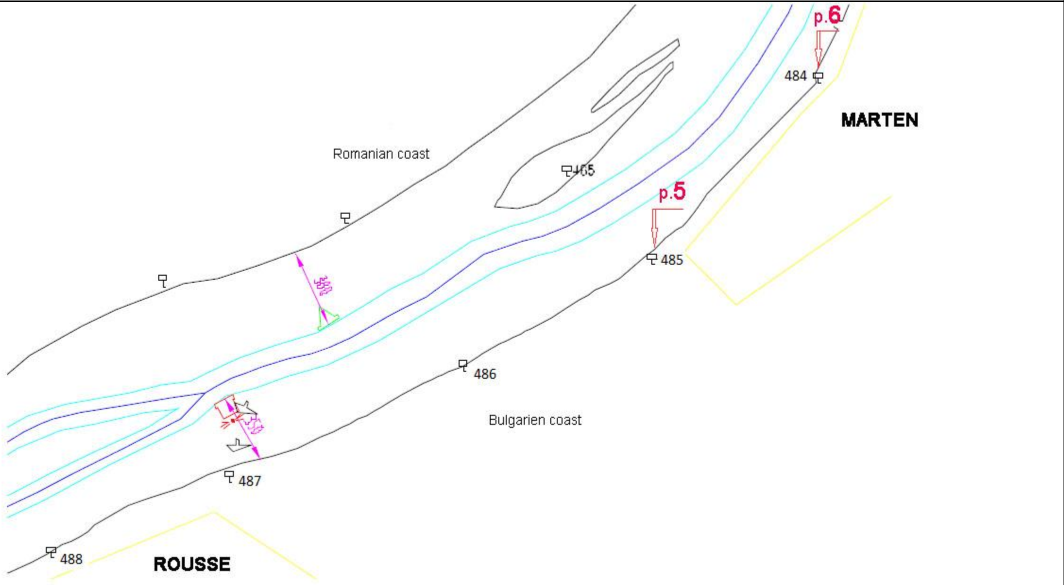


Fig. 17 **<u>LEGEND:</u>**

point 1 - **505 км** (Island “Liuliaka”) Romanian coast;

point 2 - **503 км** ((Island “Liuliaka”)) middle of the river;

point 3 **- 496 км** (Limana)) Bulgarian coast;

point 4 **- 488 km** Bulgarian coast

point 5 **- 485 km** (KTM) Bulgarian coast

point 6 **- 484 km** (Rompetrol) Bulgarian coast

DANUBE RIVER - SILISTRA AREA

(379 км - 374,5 км)

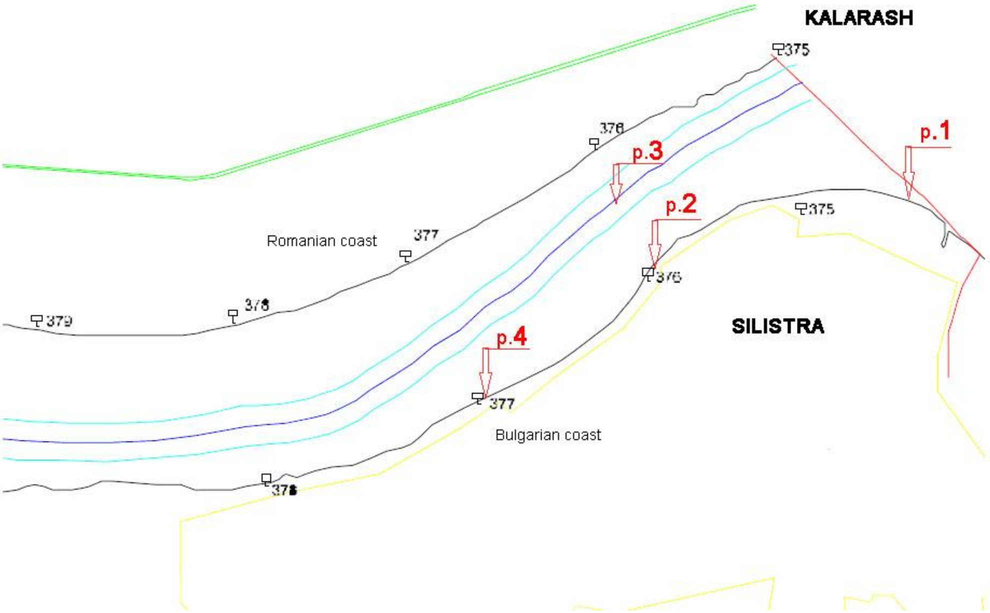


Fig. 18 **LEGEND:**

point 1 - **374,5 км** Bulgarian coast;
point 2 - **376 км** (hotel “DRASTAR”) Bulgarian coast ;
point 3 **- 376 км** (hotel “DRASTAR”) middle of the river (round fairway);
point 4 **- 377 km** (Danube park – west side) Bulgarian coast

The tests have been performed by the Bulgarian specialists from Petrol – Control – Ltd, Water, Solvents and Petroleum Testing Laboratory from Ruse - Bulgaria, an Accreditated Laboratory in compliance with the Bulgarian State Standard EN ISO/IEC 17025:2006 (Fig. 19).

СИТАЛК ЕООД (БЪЛГАРИЯ, ГР.РУСЕ, БУЛ. "ФЕРДИНАНД" 1
тел./факс: +359 82 821372 e-mail: sitalces@gmail.com)

Translation from Bulgarian

BULGARIAN ACCREDITATION SERVICE

CERTIFICATE

OF ACCREDITATION

PETROL- CONTROL- LTD

WATER, SOLVENTS AND PETROLEUM TESTING LABORATORY

Address of management: Zdravets Sever residential quarter, Rupel apartment building, entrance 3, Ruse 7005

Laboratory address: Slatina residential quarter, Ruse 7003

UIC under BULSTAT: 117618415

SCOPE OF ACCREDITATION:

Tests of:

fuels; solvents; oils; greases; coolants and wastewaters.

To test samples of:

liquid petroleum; crude oil and petroleum.

ACCREDITED IN COMLIANCE WITH THE BULGARIAN STATE STANDARD EN ISO/IEC 17025:2006

Decree no. 440 dated 11.07.07 is an integral part of the certificate of accreditation, consisting of 5 pages altogether

Valid until: 31.07.2011

BAS reg. no. 178 ЛИ

Executive director: signature- *illegible*

Elza Yaneva

Sofia 11. 07. 2007

Round seal BULGARIAN ACCREDITATION SERVICE REPUBLIC OF BULGARIA

Address of the Bulgarian Accreditation Service

The undersigned Rosen Ivanov Osenov, hereby certify the accuracy of the translation I have made from Bulgarian into English of the certificate. The translation consists of one page.

Translator: *Rosen Ivanov Osenov*

СИТАЛК ЕООД Русе
SITALCES LTD

SITALCES LTD (1 FERDINAND BLVD,
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БЪЛГАРСКА СЛУЖБА
ЗА АКРЕДИТАЦИЯ

СЕРТИФИКАТ
ЗА АКРЕДИТАЦИЯ

„ПЕТРОЛ – КОНТРОЛ" – ЕООД

„ИЗПИТВАТЕЛНА ЛАБОРАТОРИЯ ЗА ВОДИ, РАЗТВОРИТЕЛИ И НЕФТОПРОДУКТИ"

адрес на управление: 7005 Русе, комплекс "Здравец Север", бл. Рупел, вх. В
адрес на лаборатория: 7003 Русе, кв. "Слатина"

ЕИК по БУЛСТАТ: 117618415

ОБХВАТ НА АКРЕДИТАЦИЯ:

Да извършва изпитване на:

горива; разтворители; масла; смазки; течности-охлаждащи и отпадъчни води.

Да извършва вземане на проби от:

течни нефтопродукти; нефт и нефтопродукти.

АКРЕДИТИРАНА СЪГЛАСНО БДС EN ISO/IEC 17025:2006

Заповед № ......40/11.07.07...... е неделима част от сертификата за акредитация,

общо ......5... страници

Валиден до: ......31.07.2011...... БСА рег. № ......178 ЛИ..

Изпълнителен директор:

Елза Янева

София ......11.07.2007г......

1797 София, бул. „Д-р Г.М. Димитров" 52А, тел.: 02 873 5302; факс: 02 873 5303

Fig. 19 Laboratory Accreditation Certificate

Making a trial, conservation and storage of samples – general rules

Proper sampling of the water sampled is the first prerequisite for accurate characterization of its quality. The main principles to be observed when sampling the water are:

- Sample taken for analysis to reflect the conditions and place of sampling.
- Sampling, storage and transport of samples should not alter the content of the measured perimeters and components of the water.
- The sample must be sufficient and must comply with the methods used for analysis.

Sampling point is determined depending on the purpose of analysis, taking into account all circumstances affecting the composition of the sample. The aim of the analysis determined one or more serial sampling. In cases where water quality changes both in space and in time, it is applied standard sampling.

Samples for testing may be simple and mixed. Simple sample is obtained by single sampling of all the water. The analysis gives information on the properties and composition of the water at a time at a given location.

Composite sample is obtained by simple mixing of samples taken from the same place at regular intervals or taken simultaneously from different locations of the research facility. These samples characterize either the average composition of water on site, or the average stock for a period of time, or the average stock by reporting location and time of sampling.

Average sample is prepared by mixing equal parts of simple samples taken at regular intervals. This method is suitable in cases where all points of the research object are equivalent or if the point of sampling a continuous flow of water. If these conditions are not met, prepare a mean proportional sample of the various volumes of simple samples taken at different intervals.

Mixed samples are taken for a period greater than one day and in need for longer storage is preserved. They may not be prepared to determine the parameters that are easily changed (dissolved gases, pH, etc.).

The quantity of samples for analysis depends on the number of tests

- For incomplete or partial analysis -1dm^3
- For a more detailed analysis -2dm^3
- For a full analysis - 3dm^3

Containers for sampling

Most appropriate for sampling of water is clear or colorless glass made of chemically stable glass with polished stoppers or rubber stoppers.

It is allowed sampling and in plastic containers with screw caps.

The used containers for sampling must be washed. The washing becomes with concentrated hydrochloric acid, and in grease - with surfactant (surface-active substances). Highly contaminated glass bottles are washed and degreased best with dichromate mixture. Reagent containers after processing should be washed with clean water and rinsed with distilled water. Before pouring the sample containers are rinsed several times with the sample. After that they are filled up to the top to eliminate access of air, which can cause changes in the water composition. Each sample is labeled with method of preservation (if carried out). Thus prepared sample with a precise indication of the sampling site, date and time, temperature should be stored in a cool dark place.

Devices and appliances for the sampling

Most often, samples can be taken directly with a bottle. In the specific cases are used different appliances - often to take water samples from different depths is used so called batometar (Meyer's utensil). Special containers are used for sampling, in which water can come into contact with air, for sampling of the surface layer contaminated with petroleum products and others. All devices and appliances are described in relevant standards.

Sampling from different sources

Sampling of flowing water (rivers, streams)

The samples are taken from sites with the most intensive flow, 20-30 cm below the water surface. Taking both, single and serial, simple or composite samples from the middle and on both sides of the shore.

In special studies, samples are taken from various locations in the cross section of the stream. In this case is selected verticals in which sampling is done at different depths. Simultaneously it's measured flow velocity in the relevant posts.

There are basic rules for making a trial of the water from different water sources, lakes, biologic lakes and waste waters, but they are not included in the purpose of this project.

Making trails of water which contains oil-products.

The oil products which the water source contains could be found in different conditions – soluble in water, emulsified, connected (adsorbed over a different substance or sludge) and floating on its surface in the shape of a film or a layer. It defines the different ways of making trials. The trials of water containing oil products whose shape is a film could be done by a special device which can not be submersed and whose aim is only to touch the water surface. The general trail include the external film of the oil product his adjacent water layer whose altitude is equal to the sampling part of the device. The results found after an analysis has been done could be presented in mg of oil product per 1 m^2 of the water surface.

In making trails of water surfaces some places which have peaceful (quiet) surfaces are selected and then the surface layer shouldn't be mixed with the water layers below.

The basic principles should be observed in making trails when different depths are selected. The results found after an analysis has been done could be presented in mg/dm^3.

In making trials of water surfaces when the oil products should be considered it is good when glass vessels whose stoppers are polished to be used. Using of plastic vessels is not recommended (well). In making trials of water the vessels shouldn't be swilled in advance with the tested water, because it can gives errors in the final results.

Conservation of the trials

Often, in the practice it is not possible a quick analysis of the water trials to be done, which is associated with longer periods of time these trials should be saved and transported after that. In this case to keep the water's components and also the water's properties to stay the same as when the trails have been done it is necessary for them to be conserved.

When the water trials have not been conserved some different biochemical processes will start running, but it will not be the same as if that have happened in a real background, because then the water composition - pH, the quantity of the oxygen – O_2, the anionic content, the turbidity, the transparency, etc. will be changed. Even if a conserving tool is used, the impact of some of the water's components couldn't be fully prevented. In addition, for some particular cases it is not possible for the trails to be conserved. That's why it is recommended the water trials to be analyzed when the following instructions are taken into account:

A) immediately (at the places where the trials have been done or into the closest laboratory);

B) faster (in 2 hours after the trials have been made);

C) on the same day (not later than 12 hours after the trials have been done);

D) long (later than 12h after the trials have been done).

A general device for conserving does not exist yet and that's why the water trial has to be divided into different bottles for each of the tests.

The whole base data (information) found when the water trails have been done should be indicated into the concrete analysis protocol.

The conditions of making water trails/tests and the methodology in determining the indicators which are the subject of our investigation are presented in table 8.

Table 8

№	Indicators	A way of conserving	Treatment of the trial	Normative document of analysis and measuring devices
1	Extracting: TPH, oils, fatties;	It is not able to be conserved. In determining of mineral oils and fatties -5cm^3 concentrated trial of H_2SO_4 (1:1) /dm$^{3.}$	The trial should be collected in wide-angular glass vessels It can be faster determined	BSS EN ISO 9377:2004 Private methodology Petrol-control, Ltd. Gas chromatography Hewlett-Packard HP 5980
2	pH	It is not possible to be conserved.	It should be immediately determined - in 24h. A contact between the trial and the air is intolerable.	ASTM D 1293-99(2005) Private methodology Petrol-control, Ltd. pH meter, type MV 88
3	Turbidity	It is not possible to be conserved It should be kept in dark places The trial is 2-4 cm^3 $CHCl_3$ / dm^3	It can be determined in 12h It can be determined in 24h The trail should be shaken before an analysis to be done	BSS EN ISO 7027:2001 Private methodology Petrol-control, Ltd. Spectrophotometer Spekol 11- Carl Zeiss Jena-Germany and also a scanning spectrophotometer whose type is DR 3800 Germany
4	Transparency	It is not possible to be conserved	It can be determined in 24h	Private methodology Petrol – control, ltd Centrifuge T 32 A

Brief information about tests, normative documents and measuring devices

Determination of petroleum products (TRN)

TRN term express provisionally content in the water of a polar and weakly polar compounds extractable with hexane (or petroleum ether). To determine the TRN, the following methods are used: weight, spectral and chromatographic.

Spectral methods include IR - spectroscopy, UV-spectroscopy.

Chromatographic methods are: strip chromatography, thin layer chromatography and gas-liquid chromatography. The last method is used to determine TPH with a gas chromatograph HP 5980.

Determination of pH

pH is determined colorimetrically by buffering solutions with potentciometric titration.

The first method does not require special equipment and is based on comparing the color of sample water added to it an appropriate indicator of the color buffer of known pH, containing the same amount of indicator. The method yielded precision of potentiometric one.

Potentiometric determination of pH with glass electrode is based on that the change of pH by one unit causes a potential change of the electrode with 58,1 mV at 20 C.°. The dependence pH / potential of the electrode is linear over the range pH 1 to 11 and depends on the material of the glass electrode. Determination by this method do not interfere with color, turbidity, presence of oxidants in the sample, high content of salts and the presence of oil in it.

Analysis of the samples was carried out by this method on pH meter MV 88.

Determination of turbidity (transparency).

Both indicators serve as an indirect assessment of the content of mechanical impurities in the water. In the content of suspended substances in water is determined to 3mg/dm3 transparency, and above this amount - water turbidity.

Reading to the measurement of turbidity is usually performed in photometric standard graph: concentration of SiO_2 - light absorption, thus the lightoversigth of the sample compares to that of a standard suspension of SiO_2 or kaolin.

In our conditions, turbidity is defined on Spectrophotometer Spekol 11 Carl Zeiss Jena, Germany, and type spectrophotometer DR 3800.

Determination of sediments

The sediments represent mechanical impurities in the water with different backgrounds - mineral, mineral-organic or organic.

The most reliable method for determining the quantity of sludge is filtering through a filter of appropriate porosity and weight determination of the amount of retained substances from the filter.

Indirectly (not exactly), but faster the sludge is carried out on turbidity indicator (transparency) of water.

Sediments of the samples from the Danube defined weighting method and indicator "turbidity”.

The test results are object to the protocols No.601 – 610 and the chemical characteristics obtained are presented in the following table 92:

Table 9

Crt no.	Date	Km	Protocol no.	Turbidity [mg/l]	Sediments [%]	pH [%]	Solids [mg/l]	Petrol [mg/l]
1	19.05.2011	374,5	601	52,9	1,85-2,15	7,18	1630	<0,5
2	19.05.2011	376	602	95,8	2,15-3,10	7,25	1996	<0,5
3	19.05.2011	376	603	74,3	1,15-2,0	7,22	978	<0,5
4	19.05.2011	377	604	86,9	1,75-2,45	6,88	1537	<0,5
5	26.05.2011	505	505	97,5	2,35-3,28	8,12	2976	<0,5
6	26.05.2011	503	606	112,3	3,82-4,25	7,65	3739	<0,5
7	26.05.2011	496	607	87,3	1,15-2,3	7,78	1735	<0,8
8	28.05.2011	488	608	7,6	0,87-1,12	8,25	58,7	<0,7
9	28.05.2011	485	609	38,6	3,25-5,75	8,22	178,3	9,8
10	28.05.2011	484	610	12,7	0,95 – 1,58	8,35	39,7	2,85

Atached to this Study are the Protocols for the water tests performed in those 10 locations (Tabel 10):

Tabel 10

Crt. No.	Location/Sample/ Date of sampling	Protocol no./Date
1	Area Silistra. Sample № 1 - **374.5 km**; Collector - left coast/19.05.2011	**601 / 02.06.2011**
2	Area Silistra. Sample № 2 - **376 km**; hotel “Drasrar” - left coast/19.05.2011	**602 / 02.06.2011**
3	Area Silistra. Sample № 3 - **376 km;** hotel “Drasrar” – middle/19.05.2011	**603 / 02.06.2011**
4	Area Silistra. Sample № 4 - **377 km**; left coast/19.05.2011	**604 / 02.06.2011**
5	Area Ruse. Sample № 1 - **505 km**; left coast/26.05.2011	**605 / 02.06.2011.**
6	Area Ruse. Sample № 2 - **503 km**; island Luliaka/ Romanian coast middle/.26.05.2011	**606 / 02.06.2011**
7	Area Ruse. Sample № 3 - **496 km**; Yacht club-Firth/26.05.2011	**607 / 02.06.2011.**
8	Area Ruse. Sample № 4 - **488 km**; Duty-free zone/28.05.2011	**608 / 03.06.2011**
9	Area Ruse. Sample № 5 - **485 km**; Bay between HIC and Duty-free zone/28.05.2011	**609 / 03.06.2011**
10	Area Ruse. Sample № 6 - **484 km**; Wharf-ROMPETROL Bulgaria Ltd/28.05.2011	**610 / 03.06.2011**

3.2.4. Selection of materials. Corrosion and Wear Properties Analysis

3.2.4.1. Introduction in Corrosion of Metals

Corrosion is an economic enemy of huge proportions. Its enormous annual cost defies accurate accounting, but the efforts to prevent or mitigate its destructive effects are more easily accounted for in monetary terms. These preventive measures occupy the best skills of thousands of corrosion engineers and technicians, and the materials and energy used to combat corrosion result in annual costs measured in tens of billions of dollars. When the corrosion is accompanied by wear, the implications are more severe.

Most production organizations employ small groups to devote full time to preventing corrosion. These corrosion engineers install and operate corrosion control devices, make observations, participate in tests, and report results and a better understanding of the subject will help promote the conditions that are essential to corrosion control efforts.

Usual metals used in the construction of facilities are subject to corrosion. This is due to the high energy content of the elements in metallic form. In nature, most metals are found in chemical combination with other elements. These metallic ores are refined by man and formed into metals and alloys. As the energy content of the metals and alloys is higher than that of their ores, chemical re-combination of the metals to form ore like compounds is a natural process.

Considering the main subject in this project – the design of a centrifugal separator for oil-water and solid particles mixtures – the materials used are of great interest. Here, the corrosion is accompanied by wear and the implications are more severe. In the following paragraphs we present the theoretical considerations that permitted us to select the most reliable solutions, in the particular service conditions of a centrifugal separator.

3.2.4.2. Metals Corrosion – General Presentation

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localized zones so as to give a cracklike structure, very considerable weakening may result from quite a small amount of metal loss;

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft);

3. Loss of time in availability of profile-making industrial equipment;

4. Reduced value of goods due to deterioration of appearance;

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion);

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface;

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products;

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", Icor.

Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface. The most common and important electrochemical reactions in the corrosion of iron are thus:

$Fe \rightarrow Fe^{2+} + 2e$ Anodic reaction (corrosion) (1)

$2H^+ + 2e \rightarrow H2$ Cathodic reactions (simplified) (2a)

or

$H_2O + 1/2\ O_2 + 2e \rightarrow 2OH^-$ (2b)

Reaction 2a is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction 2b. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$, iron (II) hydroxide

Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish color due to partial oxidation in air.

$2Fe(OH)_2 + H_2O + 1/2\ O_2 \rightarrow 2Fe(OH)3$, hydrated iron (III) oxide

Further hydration and oxidation reactions can occur and the reddish rust that eventually forms

is a complex mixture whose exact constitution will depend on other trace elements which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be “passive”. An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures.

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e$$

Certain factors can tend to accelerate the action of a corrosion cell. These include:

(a) Establishment of well-defined locations on the surface for the anodic and cathodic reactions. This concentrates the damage on small areas where it may have more serious effects, this being described as “local cell action”. Such effects can occur when metals of differing electrochemical properties are placed in contact, giving a “galvanic couple”. Galvanic effects may be predicted by means of a study of the Galvanic Series which is a list of metals and alloys placed in order of their potentials in the corrosive environment, such as sea water. Metals having a more positive (noble) potential will tend to extract electrons from a metal which is in a more negative (base) position in the series and hence accelerate its corrosion when in contact with it. The Galvanic Series should not be confused with the Electrochemical Series, which lists the potentials only of pure metals in equilibrium with standard solutions of their ions. Galvanic effects can occur on metallic surfaces which contain more than one phase, so that “local cells” are set up on the heterogeneous surface. Localized corrosion cells can also be set up on surfaces where the metal is in a varying condition of stress, where rust, dirt or crevices cause differential access of air, where temperature variations occur, or where fluid flow is not uniform.

(b) Stimulation of the anodic or cathodic reaction. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion. Sodium chloride is encountered in marine conditions and is spread on roads in winter for de-icing. Quite small concentrations of sulphur dioxide released into the atmosphere by the combustion of fuels can dissolve in the invisibly thin surface film of moisture which is usually present on metallic surfaces when the relative humidity is over 60-70%. The acidic electrolyte that is formed under these conditions seems to be capable of stimulating both the anodic and the cathodic reactions. In practical terms it is not usually possible to eliminate completely all corrosion damage to metals used for the construction of industrial plant. The rate at which attack is of prime importance is usually expressed in one of two ways:

(1) Weight loss per unit area per unit time, usually mdd (milligrams per square decimeter per day)

(2) A rate of penetration, i.e. the thickness of metal lost. This may be expressed in American units, mpy (mils per year, a mil being a thousandth of an inch) or in metric units, mmpy (millimetres per year).

Taking as an example the corrosion of heat exchanger tubes in industrial cooling water a typical corrosion rate in untreated water would be 40-50 mpy (210-260 mdd); the use of a corrosion inhibitor could reduce this to less than 5 mpy (26 mdd). The mild steel tubing used in heat exchangers is a maximum of 200 thousandths of an inch thick, thus with corrosion rates of 40-50 mpy in untreated water, severe problems might be expected within four or five years. If suitable water treatment with corrosion inhibitors is used a life of at least twenty years might be expected. This, of course, is ignoring the fact that at some time before the metal corrodes away the tubing may have thinned to a point where its required mechanical strength is not attained. When designing equipment for a certain service life engineers often add a “corrosion allowance” to the metal thickness, permitting a certain amount of thinning before serious weakening occurs. In a cooling water system the factors influencing the rate of attack are:

(a) the condition of the metal surface

Corrosion debris and other deposits - corrosion under the deposits, with a possibility of pitting (severe attack in small spots)

(b) the nature of the environment

pH - in the range of 4-10 corrosion rate is fairly independent of pH, but it increases rapidly when the pH falls below 4.

Oxygen content - increase in oxygen concentration usually gives an increase in corrosion rate.

Flow rate - increased water flow increased oxygen access to the surface and removes protective surface films, so usually increases corrosion, but can sometimes improve access for corrosion inhibiting
reactants.

Water type - very important, in general low corrosion rates are found with scale-forming (hard) waters.

Aggressive ions which accelerate corrosion are Cl^-, SO_4^{2-} but quite complex interactions may occur between the various dissolved species in natural waters.

3.2.4.3. Characteristic Environment of Centrifugal Separator

Two types of corrosive agents are present in the service of the centrifugal separator:

-liquid mixture of **water and oil**;

-**solid particles** trained by the mixture flow that induce wear, rather than corrosion. The corrosion phenomena are stimulated by solid particles wear, by affecting the surface quality and removing the protective layer of metal oxides or coatings.

During the pause periods the separator is exposed to the atmospheric **air, containing water vapors**.

Water

In the first category, oil is not very corrosive by itself but it’s impurities and the water (containing or not salts) are deleterious.

One of the main contributing factors which causes corrosion is **water** and corrosion can hardly occur without it. Water, which is also called the universal solvent, can extract enough chemicals from diesel or gasoline to start corrosion. Water can create the right environment for certain bacteria, which can also cause corrosion. Water in conjunction with free oxygen dissolved in water oxidizes (rusts) the steel. The oxidation process will continue as long as there is free (dissolved) oxygen present in water. Rainwater and water condensation from air can continuously supply the water with needed oxygen to oxidize the steel components.

Another problem associated to the water corrosion is the presence of microorganisms. Active microbiologically influenced corrosion of metal due to bacteria is quite complex. It can involve several species of microorganisms and is affected by temperature, pH and other factors. Water in combination with the hydrocarbon fuel can serve as a medium to support the growth of various microorganisms. *Anaerobic bacteria* can survive in the oxygen-free environment existing at the fuel water interface of the storage tank. These microbes utilize the oxygen bound up in compounds for their metabolic oxygen needs rather than relying on the free oxygen dissolved in water. Different forms of bacteria can thrive in fuels containing water and, as a result of their metabolism, different chemicals including sulfuric and hydrogen sulfide acids are formed which cause severe corrosion in steel tanks. Colonies established by microbes on the sidewalls and bottoms of fuel storage tanks are called plaques. These plaques can often be the sites of MIC of the underlying metal. Even changing materials to stainless steel won't help here. A one-eighth inch thick 304 stainless steel plate has been observed to perforate in less than a month when bacterial corrosion occurs.

Oil

As we mentioned above, **impurities in oil** are very destructive corrosive agents. The most important is sulphur, present by gaseous H_2S form (hydrogen sulphide). H_2S and water make hydro sulfuric acid (H_2S). The hydro sulfuric acid will further dissociate to H^+ and HS^- ions /3/.

$$H_2S(g) \rightarrow H_2S(aq) \rightarrow H^+ + HS^- \qquad (1)$$

The H^+ ions will reduce the pH in the solution. Hydro sulfuric acid is a week acid, since only a small part of the acid will dissociate to ions. But, large concentration of H_2S combined with a small resistance to dissociate to ions, make the reduction of hydrogen to an effective reduction process.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

The electrons comes from oxidation of the metal.

$$M \rightarrow M^{2+} + 2e^- \qquad (3)$$

Having the above reactions mean that H_2S corrosion is present. This type of corrosion is general corrosion in the presence of hydro sulfuric acid and may provide high rate of corrosion for carbon steel. It has been estimated that H_2S alone is responsible for about 20% of metal corrosion losses in the petroleum industry. However, H_2S corrosion is far less common than CO_2 corrosion. A second effect of H_2S corrosion is mesa (carbon dioxide) corrosion.

Carbon dioxide (CO_2) is a normal substance in oil. CO_2 and *water* make carbonic acid H_2CO_3. The carbonic acid will further dissociate to H^+ and HCO_3^- ions (bicarbonate). This may cause CO_2 corrosion. The second effect of CO_2 is that carbon acid and steel makes a surface layer of iron carbonate $FeCO_3$ above a critical temperature called the scaling temperature. The layer is nobler than steel and may reduce the corrosion at higher temperature (opposite to other corrosion mechanisms). This is accounted for in the Norsok M506 corrosion rate model. Damages in the iron carbonate layer results in severe pitting corrosion. Corrosion rate of 10-20 mm/year has been observed in tubing made of ordinary steel under bad conditions. This localized attack produces mesa-like features by corroding away the active regions and leaving the passive regions relatively free of corrosion. The surface profile look like the mesas produced in rock by wind and water erosion. A similar effect will take place when iron sulphide (FeS) is made, which is a noble scale that tends to cause a local acceleration of the corrosion (galvanic corrosion).

Not all of the hydrogen sulfide is converted into hydro sulfuric acid when mixing water and hydrogen sulfide. Some hydrogen sulfide stays as H_2S molecules. Increased pressure and hydrogen sulfide concentration makes more hydro sulfuric acid.

Partial pressure is the pressure that would be exerted by a single component of gas if present alone, at the same temperature and in the same volume occupied by the mixture. H_2S partial pressure is dependent on the total pressure and the H_2S concentration and can be calculated in two ways (H_2S in gas phase):

$$H_2S_{PP} = (\text{Total pressure x } H_2S \text{ in mole \%}) /100 \qquad (4)$$

$$H_2S_{PP} = (\text{Total pressure x } H_2S \text{ in ppm}) /10^6 \qquad (5)$$

Increased H_2S partial pressure increases the susceptibility to H_2S corrosion. A general rule of thumb for the corrosivity for steel, low alloy steels (max 5% alloying elements) and cast irons is:

Table 11: Corrosivity versus partial pressure of H_2S

H_2S partial pressure	**Corrosivity**
< 0.003 bar (0.05 psi)	Sweet and non-corrosive environment
> 0.003 bar (0.05 psi)	Sour and corrosive operating environment

Not all of the hydrogen ions H^+ will be reduced to H_2 during the corrosion process. The presence of hydrogen sulphide at the surface of a metal will support discharging of H^+ ions to atomic hydrogen (H^0), resulting in increased absorption of atomic hydrogen into the metal.

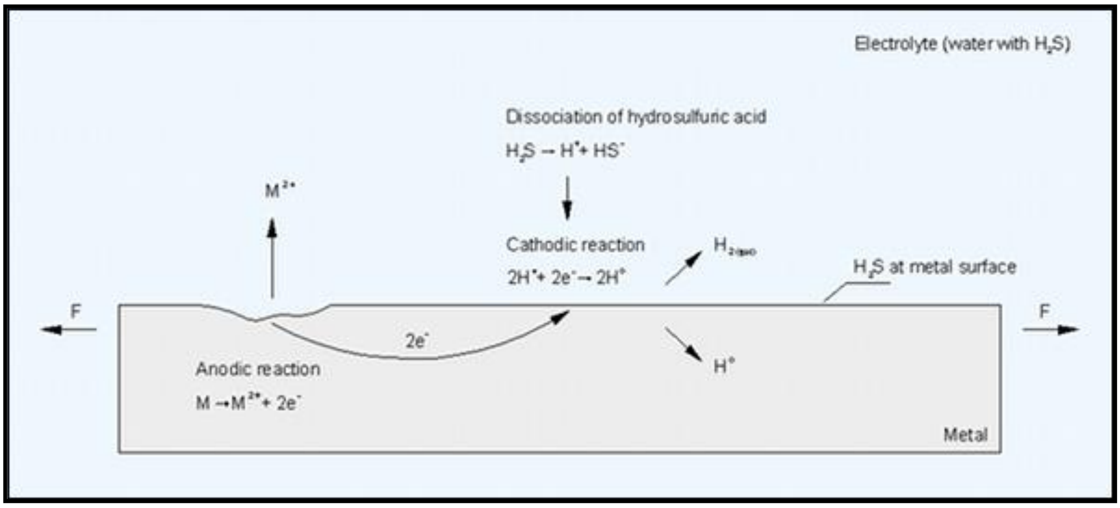


Fig.20: Absorption of atomic hydrogen into the metal

Atomic hydrogen diffuses into the metal. Metal hydrides will be precipitated when a limit is passed. The formation of hydrides will reduce the ductility and deformability of the metal. The metal will crack when exposed to tensile stresses (like external loads, residual from cold-forming or residual from welding). The sulphide stress cracking (SSC) process is very rapid and has been known to take as little as a few hours for a crack to form and cause a catastrophic failure. SSC limits the use of hardenable high-strength metals for service in contact to oil.

SSC is a function of the atomic hydrogen concentration, which will be increased at low pH values. Hydrogen absorption strongly decreases above pH 8. If the pH is maintained in the 10 to 11 range – even high-strength steels can be used.

Materials that can be used

- Carbon and low alloy steels with hardness below 22 HRC is acceptable in services concerning indirect contact to the oil-water mixtures and in surface protection conditions;

- Austenitic stainless steels are recommended for direct contact to the corrosive agents but controlling their chloride content;
- High resistant materials are Hastelloy C276, Inconel 625 and 6Mo (in general alloys with high content of Ni, Cr, Mo, W and Ni) are strongly recommended but they are very expensive;
- Martensitic stainless steels involve medium risk;
- Hydrogen diffusion rate is much lower in duplex (ferrite+austenite) stainless steels than in martensitic stainless steels;
- Titanium is susceptible to hydrogen embrittlement, but depends on the oxide film; it is very expensive, too.

Rules for materials selecting

Whether a metal can be used in a oil-water environment or not, is decided by a pH/ ppH_2S diagram (called domain diagrams).

Carbon steels and low alloy steels

A domain diagram for carbon- and low alloyed steels is shown in the figure below. Other alloys will have other configurations.

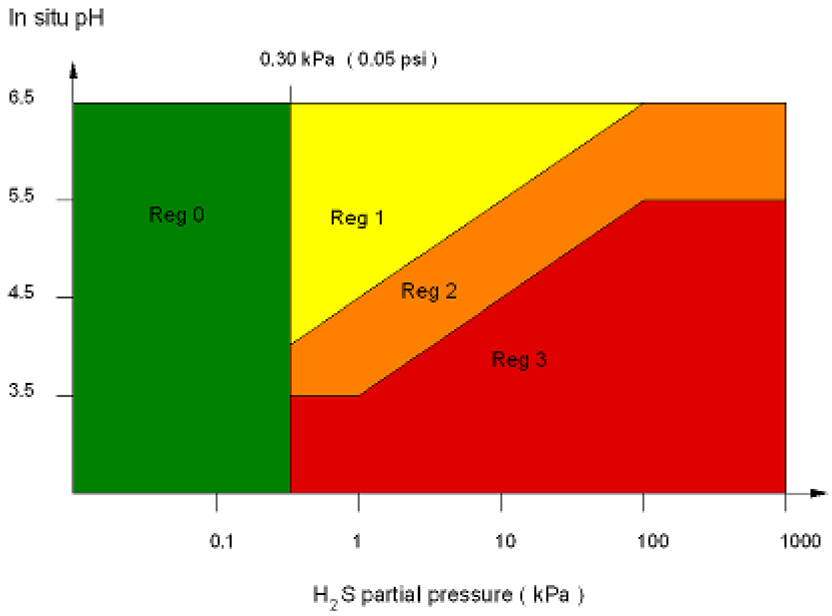


Fig. 21: Domain diagram for carbon steel, low alloyed steels and cast irons

Region 0 defines the area where normally no precautions are required. Only steels that are highly susceptible to SSC may crack. Some very high strength steels (above 965 MPa) may also crack by hydrogen stress cracking (HSC) in aqueous environments without H_2S.

Region 1 defines the area where no special metallurgical precautions are required, only properties for suitable materials. Examples of acceptable materials are AISI 4130, AISI 4140 and AISI 4145 in the quenched and tempered condition with yield strength below 896 MPa and hardness below 30 HRC.

Region 2 defines the area where also critical judgment concerning metallurgical requirements has to be made. Examples of acceptable materials are AISI 4130, AISI 4140 and AISI 4145 in the quenched and tempered condition with yield strength below 760 MPa and hardness below 27 HRC.

Region 3 defines the area where SCC may occur. In this region, the temperature must be clarified in addition to hardness, heat treatment, pH and H_2S partial pressure. One example of an acceptable material is the alloy API 5 AX, grade P-110, that can be used in region 3 when continuously exposed to a temperature in excess of 80ºC (susceptible to SSC at room temperature). The material must further be quenched and tempered with maximum yield below 965 MPs (140 ksi). Determination of the region and material requirements should be performed by experts only.

Stainless steels

An important observation is that the presence of chlorides in the oil-water mixture changes fundamentally the domain diagrams for stainless steels, comparing to carbon or low alloyed steels. The general lines for stainless steels domain diagrams are presented bellow.

- The domain diagrams assumes no oxygen;
- All stainless steels will have a lower pH limit independent of the H_2S partial pressure;
- The amount of chlorides has a large effect on the cracking resistance for some alloys.

Domain diagrams are typical made for different chloride ion concentrations. Chloride ion concentration in the range of 1000 to 1500 ppm is often used for condense water. The chloride ion concentration in formation water is normally much higher. Domain diagram that includes chlorides includes the effect that the oxide layer may be broken down by the chloride ions. It will also have the effect that SCC becomes an active mechanism at higher temperatures. The SCC effect will accelerate when dissolved oxygen is present in the water.

A more detailed analyze of the stainless steels behavior in contact to oil-water mixtures is presented later in this work.

3.2.4.4. Corrosion Behavior of Stainless Steels

Mechanism of Corrosion Resistance

The mechanism of corrosion protection for stainless steels differs from that of carbon steels and most other metals. In these other cases, the formation of a barrier of the true oxide separates the metal from the surrounding atmosphere. The degree of protection afforded by such an oxide is a function of the thickness of the oxide layer, its continuity, its coherence and adhesion to the metal and the diffusivities of oxygen and metal in the oxide. In high temperature oxidation, stainless steel use a generally similar model for corrosion protection. However, at low temperatures, stainless steels do not form a layer of true oxide. Instead, a passive is formed. One mechanism that has been suggested is the formation of a film of hydrated oxide, but there is not total agreement on the nature of the oxide complex on the metal surface. However, the oxide film should be continuous, nonporous, insoluble and self-healing if broken in the presence of oxygen.

Passivity exists under certain conditions for particular environment. The range of conditions over which passivity can be maintained depends on the precise environment and on the family and composition of the stainless steel. When conditions are favorable for maintaining passivity, stainless steels exhibit extremely low corrosion rates. If passivity is destroyed under conditions that do not permit restoration of the passive film, then stainless steel will corrode much like a carbon or low alloy steel.

The presence of oxygen is essential to the corrosion resistance of a stainless steel. The corrosion resistance of stainless steel is at its maximum when the steel is boldly exposed and the surface is maintained free of deposits by a flowing bulk environment. Covering a portion of the surface produces an oxygen-depleted region that is anodic relative to the well-aerated boldly exposed surface and a higher level of alloy content in the stainless steel is required to prevent corrosion.

With appropriate grade selection, stainless steel will perform for very long times with minimal corrosion but an inadequate grade can corrode and perforate more rapidly than a plain carbon steel that will fail by uniform corrosion. Selection of the appropriate grade of stainless steel is then a balancing of the desire to minimize cost and the risk of corrosion damage.

General Corrosion Characteristics of Stainless Steel Families

Stainless steels are classified into the following five families, determinated by the main microstructural constituent (matrix), at room temperature:

- austenitic;
- ferritic;
- martensitic;
- duplex (ferrite+austenite);
- precipitation hardening (PH).

Fig. 22 shows the evolution of stainless steels grades, starting from 304 grade and Table 12 contains the chemical composition of the most used grades.

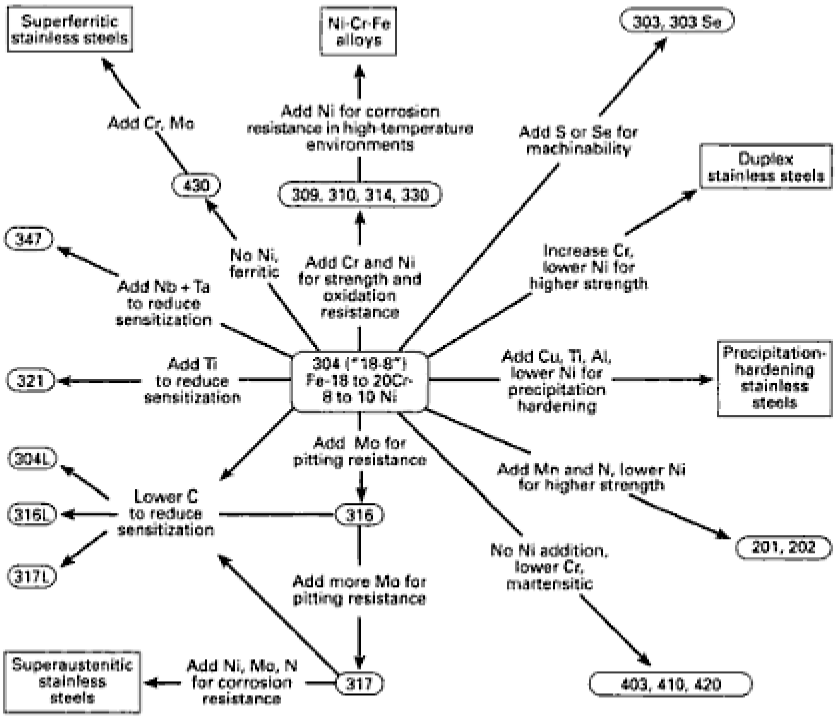
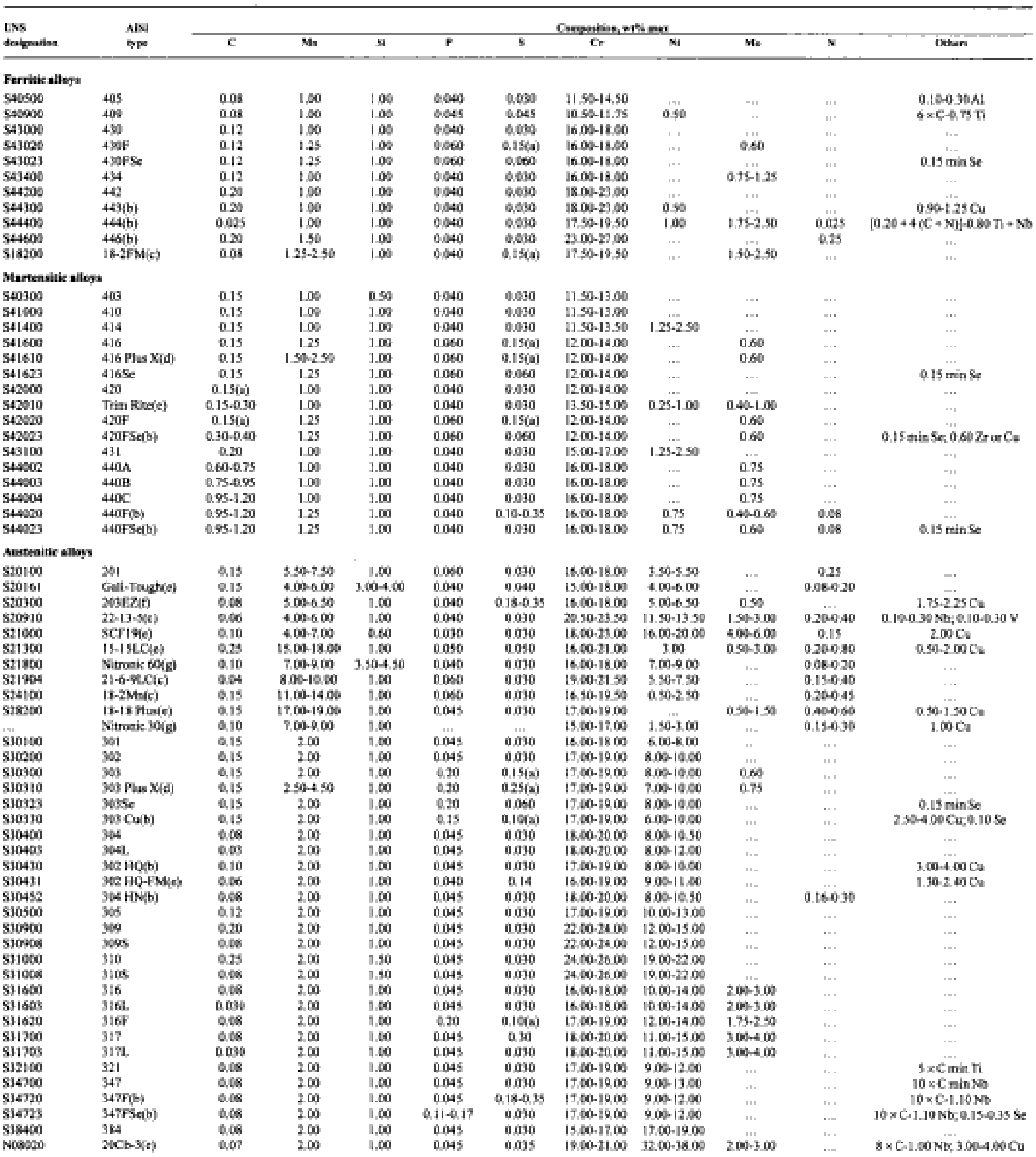


Fig. 22 Evolution of stainless steels grades

Austenitic Stainless Steels

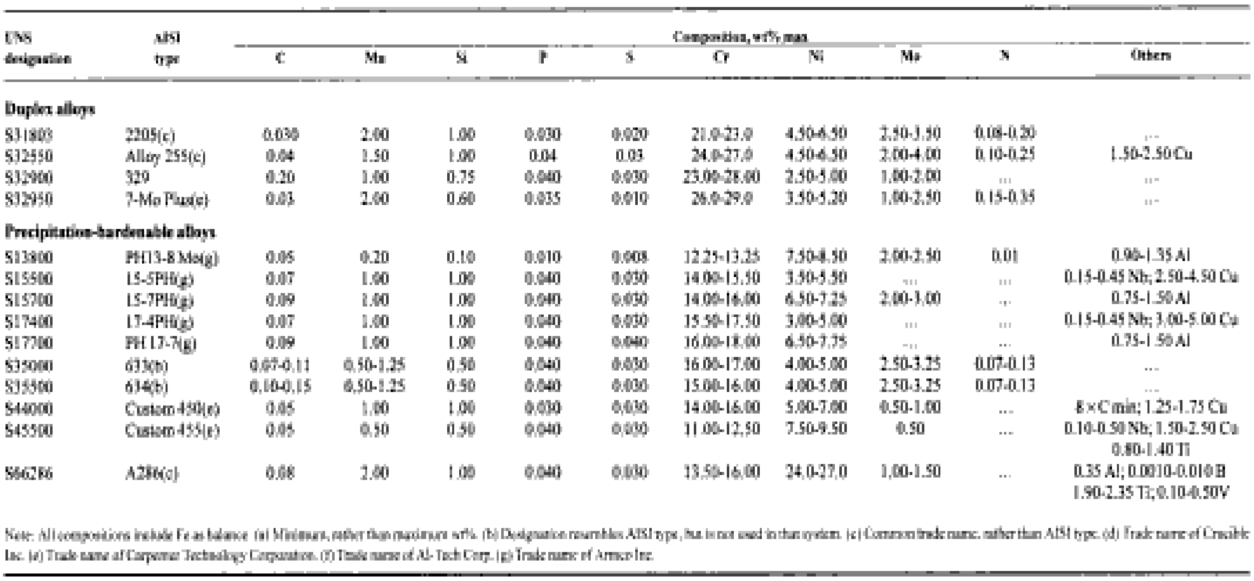
Austenitic stainless steels were developed for use in both mild and severe corrosive conditions. They are also used at temperatures that range from cryogenic temperatures, where they exhibit high toughness, to elevated temperatures, where they exhibit good oxidation resistance. The most used austenitic stainless steel is 304 (18Cr-8Ni) and the evolution was just in the addition of molybdenum (for pitting corrosion resistance) and nitrogen (for austenite stabilization). With the nitrogen addition, it is possible to produce austenitic grades with up to 6% Mo for improved corrosion resistance in chloride environments (see the Table 13 below containing “superaustenitc grades”). Other special grades include the high chromium grades for high temperature applications and the high-nickel grades for inorganic acid environments.

Table 12 Chemical composition of the most used stainless steels



UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
Ferritic alloys											
S40500	405	0.08	1.00	1.00	0.040	0.030	11.50-14.50	...	...	...	0.10-0.30 Al
S40900	409	0.08	1.00	1.00	0.045	0.045	10.50-11.75	0.50	...	...	6 × C-0.75 Ti
S43000	430	0.12	1.00	1.00	0.040	0.030	16.00-18.00	...	...	...	...
S43020	430F	0.12	1.25	1.00	0.060	0.15(a)	16.00-18.00	...	0.60	...	...
S43023	430FSe	0.12	1.25	1.00	0.060	0.060	16.00-18.00	...	...	...	0.15 min Se
S43400	434	0.12	1.00	1.00	0.040	0.030	16.00-18.00	...	0.75-1.25	...	...
S44200	442	0.20	1.00	1.00	0.040	0.030	18.00-23.00	...	...	...	...
S44300	443(b)	0.20	1.00	1.00	0.040	0.030	18.00-23.00	0.50	...	...	0.90-1.25 Cu
S44400	444(b)	0.025	1.00	1.00	0.040	0.030	17.50-19.50	1.00	1.75-2.50	0.025	[0.20 + 4 (C + N)]-0.80 Ti + Nb
S44600	446(b)	0.20	1.50	1.00	0.040	0.030	23.00-27.00	...	...	0.25	...
S18200	18-2FM(c)	0.08	1.25-2.50	1.00	0.040	0.15(a)	17.50-19.50	...	1.50-2.50	...	...
Martensitic alloys											
S40300	403	0.15	1.00	0.50	0.040	0.030	11.50-13.00	...	...	...	...
S41000	410	0.15	1.00	1.00	0.040	0.030	11.50-13.00	...	...	...	...
S41400	414	0.15	1.00	1.00	0.040	0.030	11.50-13.50	1.25-2.50	...	...	...
S41600	416	0.15	1.25	1.00	0.060	0.15(a)	12.00-14.00	...	0.60	...	...
S41610	416 Plus X(d)	0.15	1.50-2.50	1.00	0.060	0.15(a)	12.00-14.00	...	0.60	...	...
S41623	416Se	0.15	1.25	1.00	0.060	0.060	12.00-14.00	...	...	...	0.15 min Se
S42000	420	0.15(a)	1.00	1.00	0.040	0.030	12.00-14.00	...	...	...	...
S42010	Trim Rite(e)	0.15-0.30	1.00	1.00	0.040	0.030	13.50-15.00	0.25-1.00	0.40-1.00	...	...
S42020	420F	0.15(a)	1.25	1.00	0.060	0.15(a)	12.00-14.00	...	0.60	...	...
S42023	420FSe(b)	0.30-0.40	1.25	1.00	0.060	0.060	12.00-14.00	...	0.60	...	0.15 min Se; 0.60 Zr or Cu
S43100	431	0.20	1.00	1.00	0.040	0.030	15.00-17.00	1.25-2.50	...	...	...
S44002	440A	0.60-0.75	1.00	1.00	0.040	0.030	16.00-18.00	...	0.75	...	...
S44003	440B	0.75-0.95	1.00	1.00	0.040	0.030	16.00-18.00	...	0.75	...	...
S44004	440C	0.95-1.20	1.00	1.00	0.040	0.030	16.00-18.00	...	0.75	...	...
S44020	440F(b)	0.95-1.20	1.25	1.00	0.040	0.10-0.35	16.00-18.00	0.75	0.40-0.60	0.08	...
S44023	440FSe(b)	0.95-1.20	1.25	1.00	0.040	0.030	16.00-18.00	0.75	0.60	0.08	0.15 min Se
Austenitic alloys											
S20100	201	0.15	5.50-7.50	1.00	0.060	0.030	16.00-18.00	3.50-5.50	...	0.25	...
S20161	Gall-Tough(e)	0.15	4.00-6.00	3.00-4.00	0.040	0.040	15.00-18.00	4.00-6.00	...	0.08-0.20	...
S20300	203EZ(f)	0.08	5.00-6.50	1.00	0.040	0.18-0.35	16.00-18.00	5.00-6.50	0.50	...	1.75-2.25 Cu
S20910	22-13-5(c)	0.06	4.00-6.00	1.00	0.040	0.030	20.50-23.50	11.50-13.50	1.50-3.00	0.20-0.40	0.10-0.30 Nb; 0.10-0.30 V
S21000	SCF19(e)	0.10	4.00-7.00	0.60	0.030	0.030	18.00-23.00	16.00-20.00	4.00-6.00	0.15	2.00 Cu
S21300	15-15LC(e)	0.25	15.00-18.00	1.00	0.050	0.050	16.00-21.00	3.00	0.50-3.00	0.20-0.80	0.50-2.00 Cu
S21800	Nitronic 60(g)	0.10	7.00-9.00	3.50-4.50	0.040	0.030	16.00-18.00	7.00-9.00	...	0.08-0.20	...
S21904	21-6-9LC(c)	0.04	8.00-10.00	1.00	0.060	0.030	19.00-21.50	5.50-7.50	...	0.15-0.40	...
S24100	18-2Mn(c)	0.15	11.00-14.00	1.00	0.060	0.030	16.50-19.50	0.50-2.50	...	0.20-0.45	...
S28200	18-18 Plus(e)	0.15	17.00-19.00	1.00	0.045	0.030	17.00-19.00	...	0.50-1.50	0.40-0.60	0.50-1.50 Cu
...	Nitronic 30(g)	0.10	7.00-9.00	1.00	...	...	15.00-17.00	1.50-3.00	...	0.15-0.30	1.00 Cu
S30100	301	0.15	2.00	1.00	0.045	0.030	16.00-18.00	6.00-8.00	...	...	...
S30200	302	0.15	2.00	1.00	0.045	0.030	17.00-19.00	8.00-10.00	...	...	...
S30300	303	0.15	2.00	1.00	0.20	0.15(a)	17.00-19.00	8.00-10.00	0.60	...	...
S30310	303 Plus X(d)	0.15	2.50-4.50	1.00	0.20	0.25(a)	17.00-19.00	7.00-10.00	0.75	...	...
S30323	303Se	0.15	2.00	1.00	0.20	0.060	17.00-19.00	8.00-10.00	...	...	0.15 min Se
S30330	303 Cu(b)	0.15	2.00	1.00	0.15	0.10(a)	17.00-19.00	6.00-10.00	...	...	2.50-4.00 Cu; 0.10 Se
S30400	304	0.08	2.00	1.00	0.045	0.030	18.00-20.00	8.00-10.50	...	...	...
S30403	304L	0.03	2.00	1.00	0.045	0.030	18.00-20.00	8.00-12.00	...	...	...
S30430	302 HQ(b)	0.10	2.00	1.00	0.045	0.030	17.00-19.00	8.00-10.00	...	...	3.00-4.00 Cu
S30431	302 HQ-FM(e)	0.06	2.00	1.00	0.040	0.14	16.00-19.00	9.00-11.00	...	...	1.30-2.40 Cu
S30452	304 HN(b)	0.08	2.00	1.00	0.045	0.030	18.00-20.00	8.00-10.50	...	0.16-0.30	...
S30500	305	0.12	2.00	1.00	0.045	0.030	17.00-19.00	10.00-13.00	...	...	...
S30900	309	0.20	2.00	1.00	0.045	0.030	22.00-24.00	12.00-15.00	...	...	...
S30908	309S	0.08	2.00	1.00	0.045	0.030	22.00-24.00	12.00-15.00	...	...	...
S31000	310	0.25	2.00	1.50	0.045	0.030	24.00-26.00	19.00-22.00	...	...	...
S31008	310S	0.08	2.00	1.50	0.045	0.030	24.00-26.00	19.00-22.00	...	...	...
S31600	316	0.08	2.00	1.00	0.045	0.030	16.00-18.00	10.00-14.00	2.00-3.00	...	...
S31603	316L	0.030	2.00	1.00	0.045	0.030	16.00-18.00	10.00-14.00	2.00-3.00	...	...
S31620	316F	0.08	2.00	1.00	0.20	0.10(a)	17.00-19.00	12.00-14.00	1.75-2.50	...	...
S31700	317	0.08	2.00	1.00	0.045	0.30	18.00-20.00	11.00-15.00	3.00-4.00	...	...
S31703	317L	0.030	2.00	1.00	0.045	0.030	18.00-20.00	11.00-15.00	3.00-4.00	...	...
S32100	321	0.08	2.00	1.00	0.045	0.030	17.00-19.00	9.00-12.00	...	...	5 × C min Ti
S34700	347	0.08	2.00	1.00	0.045	0.030	17.00-19.00	9.00-13.00	...	...	10 × C min Nb
S34720	347F(b)	0.08	2.00	1.00	0.045	0.18-0.35	17.00-19.00	9.00-12.00	...	...	10 × C-1.10 Nb
S34723	347FSe(b)	0.08	2.00	1.00	0.11-0.17	0.030	17.00-19.00	9.00-12.00	...	...	10 × C-1.10 Nb; 0.15-0.35 Se
S38400	384	0.08	2.00	1.00	0.045	0.030	15.00-17.00	17.00-19.00	...	...	...
N08020	20Cb-3(e)	0.07	2.00	1.00	0.045	0.035	19.00-21.00	32.00-38.00	2.00-3.00	...	8 × C-1.00 Nb; 3.00-4.00 Cu

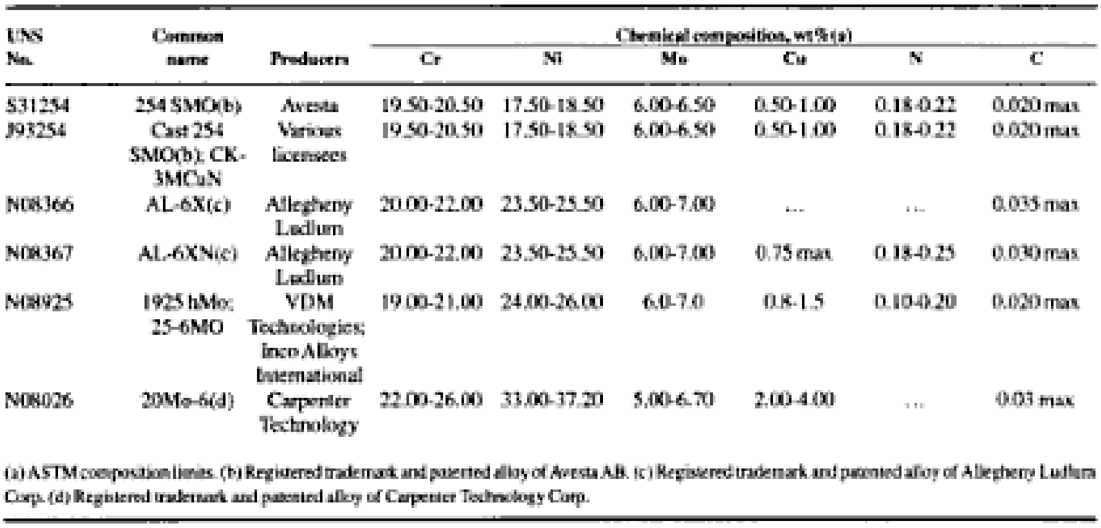
Table 12 (continuing)



UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
Duplex alloys											
S31803	2205(c)	0.030	2.00	1.00	0.030	0.020	21.0-23.0	4.50-6.50	2.50-3.50	0.08-0.20	...
S32550	Alloy 255(c)	0.04	1.50	1.00	0.04	0.03	24.0-27.0	4.50-6.50	2.00-4.00	0.10-0.25	1.50-2.50 Cu
S32900	329	0.20	1.00	0.75	0.040	0.030	23.00-28.00	2.50-5.00	1.00-2.00	...	...
S32950	7-Mo Plus(e)	0.03	2.00	0.60	0.035	0.010	26.0-29.0	3.50-5.20	1.00-2.50	0.15-0.35	...
Precipitation-hardenable alloys											
S13800	PH13-8 Mo(g)	0.05	0.20	0.10	0.010	0.008	12.25-13.25	7.50-8.50	2.00-2.50	0.01	0.90-1.35 Al
S15500	15-5PH(g)	0.07	1.00	1.00	0.040	0.030	14.00-15.50	3.50-5.50	...	...	0.15-0.45 Nb; 2.50-4.50 Cu
S15700	15-7PH(g)	0.09	1.00	1.00	0.040	0.030	14.00-16.00	6.50-7.25	2.00-3.00	...	0.75-1.50 Al
S17400	17-4PH(g)	0.07	1.00	1.00	0.040	0.030	15.50-17.50	3.00-5.00	...	...	0.15-0.45 Nb; 3.00-5.00 Cu
S17700	PH 17-7(g)	0.09	1.00	1.00	0.040	0.040	16.00-18.00	6.50-7.75	...	...	0.75-1.50 Al
S35000	633(b)	0.07-0.11	0.50-1.25	0.50	0.040	0.030	16.00-17.00	4.00-5.00	2.50-3.25	0.07-0.13	...
S35500	634(b)	0.10-0.15	0.50-1.25	0.50	0.040	0.030	15.00-16.00	4.00-5.00	2.50-3.25	0.07-0.13	...
S44000	Custom 450(e)	0.05	1.00	1.00	0.030	0.030	14.00-16.00	5.00-7.00	0.50-1.00	...	8×C min; 1.25-1.75 Cu
S45500	Custom 455(e)	0.05	0.50	0.50	0.040	0.030	11.00-12.50	7.50-9.50	0.50	...	0.10-0.50 Nb; 1.50-2.50 Cu 0.80-1.40 Ti
S66286	A286(c)	0.08	2.00	1.00	0.040	0.030	13.50-16.00	24.0-27.0	1.00-1.50	...	0.35 Al; 0.0010-0.010 B 1.90-2.35 Ti; 0.10-0.50V

Note: All compositions include Fe as balance. (a) Minimum, rather than maximum wt%. (b) Designation resembles AISI type, but is not used in that system. (c) Common trade name, rather than AISI type. (d) Trade name of Crucible Inc. (e) Trade name of Carpenter Technology Corporation. (f) Trade name of Al-Tech Corp. (g) Trade name of Armco Inc.

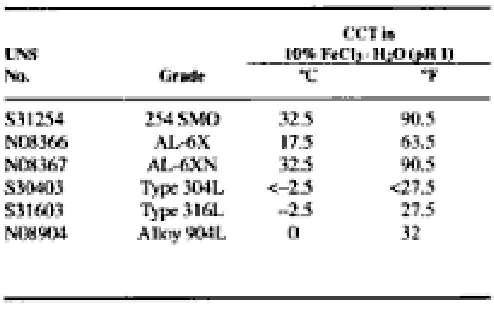
Table 13 Chemical composition of superaustenitic steels



UNS No.	Common name	Producers	Chemical composition, wt%(a)					
			Cr	Ni	Mo	Cu	N	C
S31254	254 SMO(b)	Avesta	19.50-20.50	17.50-18.50	6.00-6.50	0.50-1.00	0.18-0.22	0.020 max
J93254	Cast 254 SMO(b); CK-3MCuN	Various licensees	19.50-20.50	17.50-18.50	6.00-6.50	0.50-1.00	0.18-0.22	0.020 max
N08366	AL-6X(c)	Allegheny Ludlum	20.00-22.00	23.50-25.50	6.00-7.00	...	...	0.035 max
N08367	AL-6XN(c)	Allegheny Ludlum	20.00-22.00	23.50-25.50	6.00-7.00	0.75 max	0.18-0.25	0.030 max
N08925	1925 hMo; 25-6MO	VDM Technologies; Inco Alloys International	19.00-21.00	24.00-26.00	6.0-7.0	0.8-1.5	0.10-0.20	0.020 max
N08026	20Mo-6(d)	Carpenter Technology	22.00-26.00	33.00-37.20	5.00-6.70	2.00-4.00	...	0.03 max

(a) ASTM composition limits. (b) Registered trademark and patented alloy of Avesta AB. (c) Registered trademark and patented alloy of Allegheny Ludlum Corp. (d) Registered trademark and patented alloy of Carpenter Technology Corp.

Table 14 Critical crevice temperature (CCT) for 6 grades of austenitic steels, in 9% FeCl3 and pH1 NaOh



UNS No.	Grade	CCT in 10% $FeCl_3 \cdot H_2O$ (pH 1)	
		°C	°F
S31254	254 SMO	32.5	90.5
N08366	AL-6X	17.5	63.5
N08367	AL-6XN	32.5	90.5
S30403	Type 304L	<−2.5	<27.5
S31603	Type 316L	−2.5	27.5
N08904	Alloy 904L	0	32

The austenitic stainless steels are susceptible to sensitization to intergranular corrosion by welding or by long time thermal exposure. This exposure lead to the precipitation of chromium carbides in grain boundaries and to the depletion of chromium adjacent to these carbides. Sensitization is an important subject when weldings are going to be performed or during heat treatments and it can be delayed or prevented by using low-carbon grades (>0,03% C) or stabilized grades (321, 327). Also, there are time-temperature sensitization curves that permit to avoid combinations that promote intergranular carbide precipitation. Fig. 23 shows these curves for 304 grade austenitic stainless steel.

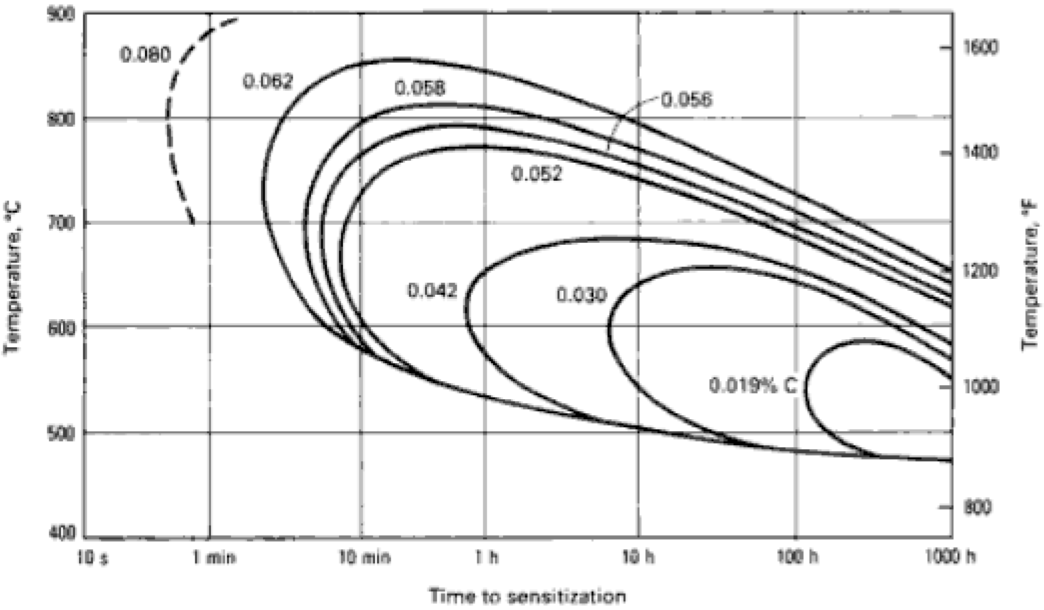


Fig. 23 Time-temperature sensitization curves for 304 grade austenitic stainless steel

Ferritic Steels

The simplest stainless steel contain only iron and chromium that is a ferrite stabilizer: therefore, the stability of the ferritic structure increases with chromium content. Ferrite has a b.c.c. structure, it is magnetic and it is characterized by high yield strength but low ductility. Ferrite shows a very low solubility of interstitial atoms like carbon and nitrogen. The ferritic steels exhibit a narrow ductile-brittle transition range and for some grades this range is above room temperature.

For the purpose of this project, ferritic steels are out of interest, because they are expensive and difficult to process.

Martensitic Steels

With lower chromium levels and relatively high carbon levels, it is possible to obtain austenite at elevated temperature and then, with accelerated cooling, to transform this austenite to martensite, which has a b.c.c.- tetragonal structure. This strong and brittle martensite can be tempered to favorable combination of high strength and good toughness. Because of the ferritic stabilizing character of chromium, the total chromium content, and thus the corrosion resistance of the martensitic grades is somewhat limited. They have far lower corrosion resistance than the austenitic grades and in most instances somewhat lower resistance than ferritic grades, particularly the superferritic alloys. In recent years,, nitrogen, nickel and molybdenum additions at lower carbon levels have produced martensitic stainless steels of improved toughness and corrosion resistance.

Duplex Stainless Steels

Duplex stainless steels are two phases alloys based on iron-chromium-nickel system. These materials typically comprise approximately equal proportion of ferrite and austenite phases in their microstructure and are characterisated by their low carbon content (<0,03%) and additions of molybdenum, nitrogen, tungsten and copper. Typical chromium-nickel content are 20 to 30% and 5-10% respectively. The specific advantages offered by duplex stainless steels over conventional 300 series stainless steels are strength (about twice that of austenitic stainless steels), chloride SCC resistance (see fig.24) and pitting corrosion resistance.

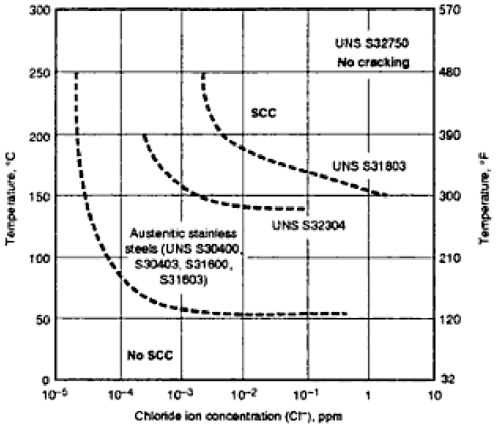
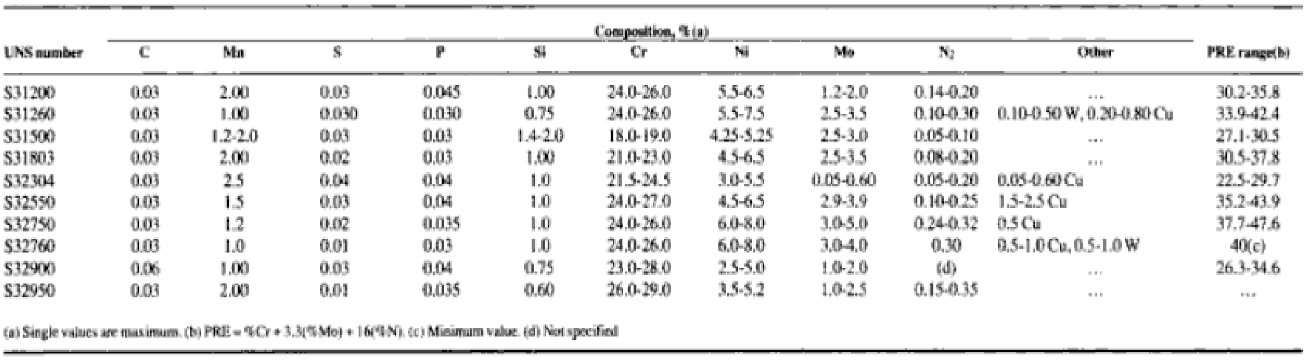


Fig. 24 Stress corrosion cracking resistance of some duplex stainless steels relative to that of austenitic steels, as a function of temperature and chloride concentration in neutral O_2 bearing solutions (aprox. 8 ppm). Test duration- 1000 hours, stress= yield strength

Table 15 Composition and pitting resistance equivalent (PRE) values of selected wrought duplex stainless steels



UNS number	Composition, % (a)										PRE range(b)
	C	Mn	S	P	Si	Cr	Ni	Mo	N_2	Other	
S31200	0.03	2.00	0.03	0.045	1.00	24.0-26.0	5.5-6.5	1.2-2.0	0.14-0.20	…	30.2-35.8
S31260	0.03	1.00	0.030	0.030	0.75	24.0-26.0	5.5-7.5	2.5-3.5	0.10-0.30	0.10-0.50 W, 0.20-0.80 Cu	33.9-42.4
S31500	0.03	1.2-2.0	0.03	0.03	1.4-2.0	18.0-19.0	4.25-5.25	2.5-3.0	0.05-0.10	…	27.1-30.5
S31803	0.03	2.00	0.02	0.03	1.00	21.0-23.0	4.5-6.5	2.5-3.5	0.08-0.20	…	30.5-37.8
S32304	0.03	2.5	0.04	0.04	1.0	21.5-24.5	3.0-5.5	0.05-0.60	0.05-0.20	0.05-0.60 Cu	22.5-29.7
S32550	0.03	1.5	0.03	0.04	1.0	24.0-27.0	4.5-6.5	2.9-3.9	0.10-0.25	1.5-2.5 Cu	35.2-43.9
S32750	0.03	1.2	0.02	0.035	1.0	24.0-26.0	6.0-8.0	3.0-5.0	0.24-0.32	0.5 Cu	37.7-47.6
S32760	0.03	1.0	0.01	0.03	1.0	24.0-26.0	6.0-8.0	3.0-4.0	0.30	0.5-1.0 Cu, 0.5-1.0 W	40(c)
S32900	0.06	1.00	0.03	0.04	0.75	23.0-28.0	2.5-5.0	1.0-2.0	(d)	…	26.3-34.6
S32950	0.03	2.00	0.01	0.035	0.60	26.0-29.0	3.5-5.2	1.0-2.5	0.15-0.35	…	…

(a) Single values are maximum. (b) PRE = %Cr + 3.3(%Mo) + 16(%N). (c) Minimum value. (d) Not specified

Note: PRE=%Cr+3,3%Mo+16%Ni

Precipitation-Hardening (PH) Stainless Steels

The PH stainless steels are chromium-nickel grades that can be hardened by an aging treatment at a moderately elevated temperature. These grades may have austenitic, semiaustenitic or martensitic crystal structures. Semiaustenitic structures are transformed from a readily formable austenite to martensite by a high temperature austenite-conditioning treatment. Some grades use cold work to facilitate transformation. The strengthening effect is achieved by adding such elements as copper and aluminum, which form intermetallic precipitates during aging. In the solution annealed condition, these grades have properties similar to those of the austenitic grades and are therefore readily formed. Hardening is achieved after fabrication within a relatively short time at 480 to 620^{0}C. The PH grades must not be subjected to further exposure to elevated temperature by welding or environment, because the strengthening can be lost by overaging of the precipitate. The PH grades have corrosion resistance generally comparable to that of chromium-nickel grades and superior to the hardenable 400-series stainless steels.

Aqueous Corrosion of Stainless Steels

In this brief overview focusing on degradation of metals and alloys in aqueous systems, the environment variables that affect corrosion are as follows:

- pH (acidity)
- Oxidizing power (electrochemical potential)

- Temperature and heat transfer
- Velocity (fluid movement)
- Solution components and their concentration

One point to bear in mind is that corrosion is a process, not a property. That distinction means that the corrosion resistance of a material depends as much on the environmental components and system dynamics to which the material is exposed as it does to the chemical composition and structure of the material itself. The discussion is not meant to be all-inclusive but to provide an overview of the complex effects that environmental variables can have on corrosion and to emphasize some of the more important relationships among them. Often, particular effects can only be deduced from carefully planned experimental testing designed to duplicate the actual system. The more understanding one has of how environmental variables might affect corrosion, the better the chances that the experiment will simulate the actual conditions. The influence of biological organisms on these environmental variables is also an important consideration.

Thermodynamics provides a theoretical framework within which the effects of several environmental variables might be pictured. In aqueous corrosion, the format often used is the potential-pH diagram, or Pourbaix diagram. The expanded portion of the potential-pH diagram of iron at 25 °C (77 °F) shown in Fig. X.6 is considered as an example of how this framework might be used .These diagrams are thermodynamic and show the most stable state of the metal in an aqueous solution. The dependence of iron corrosion on oxidizing power (electromotive force), acidity (pH), temperature, and species concentration is illustrated in Fig.25 For example, suppose the corrosion potential lies at -0.5 V standard hydrogen electrode (SHE) at a pH of 8. The most stable state of iron is Fe2+, indicating that iron dissolution is possible. If the pH is increased to 10 (the acidity is decreased), the most stable state becomes magnetite (Fe3O4), and most likely, the corrosion rate of iron would greatly decrease, its surface becoming oxidized. If the pH is then decreased to approximately 8.5, the most stable state (Fe2+ or Fe3O4) would depend on the concentration of the dissolved iron species. The concentration of dissolved species could influence the corrosion rate. A change in temperature would alter the entire diagram, changing both the areas of stability and the components within those areas.

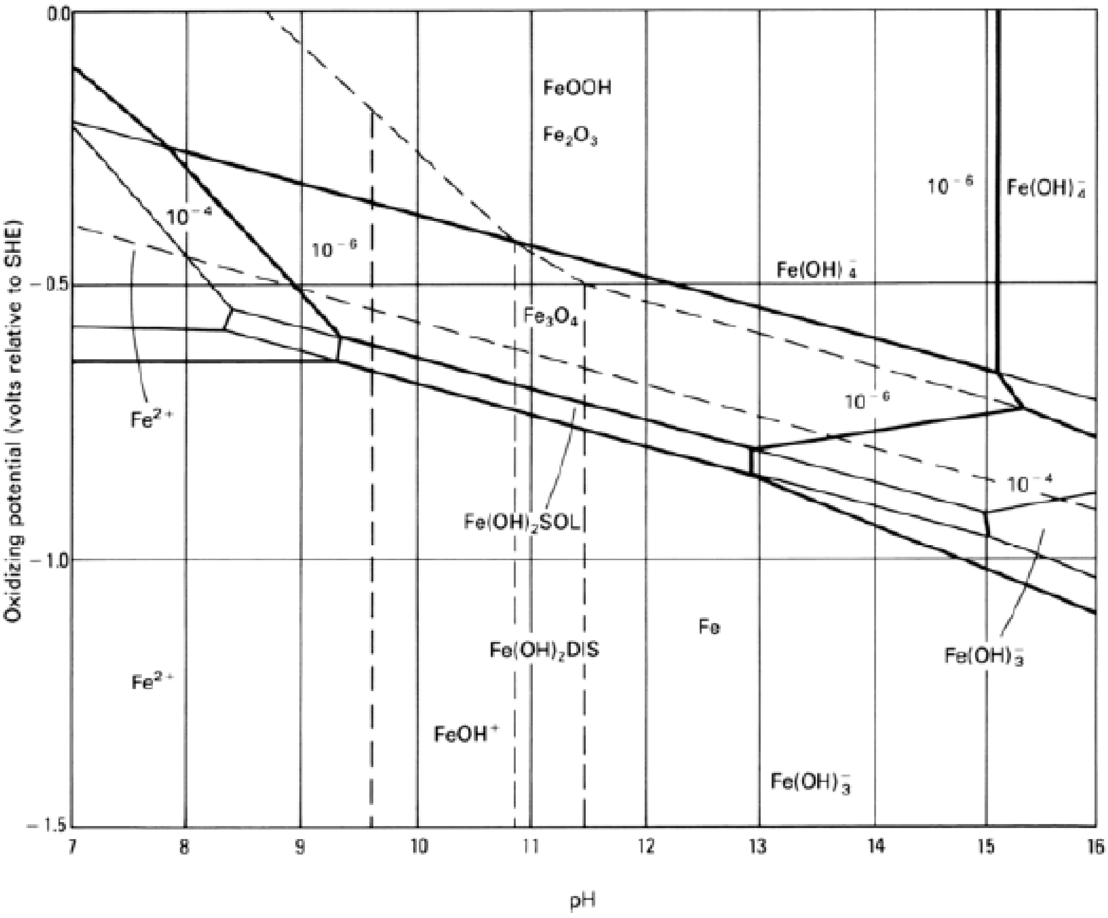


Fig. 25 Potential-pH (Pourbaix) diagram for iron at 25 °C (77 °F) in water. Ionic species are at activities of 10-6 and 10-4. SHE, standard hydrogen electrode. SOL, in solution. DIS, dissolved.

The simple example of Fig. 25 shows the dominating role that environmental variables can play in corrosion. Complex interrelationships can exist. The combined values of the variables pH, potential, concentration, and temperature not only affect corrosion but also affect the action of each variable. For example, with respect to Fig. 25 the effect of a pH change depends on the concentration of the dissolved species, and vice versa.

Contribution of pH

The important point is that the **pH effect** on corrosion of carbon steel at low pH is not simple. Knowledge of how pH affects corrosion in one acid does not necessarily translate to knowledge in another acid. Very little fundamental information is available on the effect of acid mixtures on corrosion, so kinetic equations relating corrosion rate to concentration in these systems usually do not exist. Ferritic iron-chromium alloys have been found to exhibit behavior in concentrated H2SO4 reminiscent of the behavior of carbon steel. A strong fluid velocity sensitivity has been noted in 1 *M* H2SO4 (5 to 10 wt%) for those alloys with less than 12 wt% Cr and in the 68 to 93 wt% H2SO4 range for E-Brite 26-1 (26 wt% Cr). The corrosion rate tends to be related to the rate of mass transfer of FeSO4 from a saturated film on the surface. The one difference is that the presence of oxygen may impart a pseudo passivity that can be unstable. The major point is that the presence of chromium in the alloy does not necessarily increase protection in this environment. Both chromium content and H2SO4 concentration must be considered simultaneously, especially because an 18 wt% Cr ferritic alloy tends to be under activation control in 1 *M* H2SO4 .The addition of nickel to create austenitic alloys alters this behavior in H2SO4 and eliminates, or at least diminishes, this sensitivity to fluid motion, especially in the hydrogen activity range of 10-3 to greater than 1 (pH range from approximately 3 to less than 0). At lower pH, the higher acid concentrations may produce a velocity sensitivity. Unfortunately, kinetic data are sparse on the effect of pH on the low corrosion rates expected for many of these alloys in this low pH range of -0.5 to 3. At still lower pH, the behavior is complex, and the particular literature on the alloy should be consulted. Impurities in the H2SO4 can significantly alter the corrosion resistance. The behavior of austenitic alloys in HCl is far different from that in H2SO4, even at the same pH or hydrogen ion concentration. The change from sulfate to chloride anion tends to be detrimental. The presence of the chloride ion raises the possibility of localized attack, for example crevice corrosion, pitting, and stress corrosion cracking (SCC) .

Velocity and Fluid Movement

Fluid flow rate, or fluid velocity, is also a complex variable. Its influence on corrosion depends on the alloy, fluid components, fluid physical properties, geometry in which the fluid is contained, and corrosion mechanism. These relationships are best discussed in terms of specific examples. In a number of instances, the corrosion rate is determined by the rate of transfer of a species between the surface and the fluid. This situation arises when the corrosion reaction itself is very rapid and one of the corrosion reactants or products has low solubility in the bulk fluid.

The presence of fluid flow can sometimes be beneficial in preventing or decreasing localized attack. For example, type 316 stainless steel has been shown to pit in quiescent seawater but not in moving seawater. When the seawater is moving, the mass transfer rate of oxygen is high enough to maintain a completely passive surface, but in the absence of flow, the mass transfer of oxygen is too slow, and the surface cannot remain passive. This observation indicates that sometimes, fluid velocity can be beneficial even if the corrosion rate involves the mass transfer of a reactant or product. The propensity for localized attack to occur can sometimes be decreased by maintaining sufficient fluid motion. Under other circumstances, fluid flow has been reported to cause a type of erosion of a surface through the mechanical force of the fluid itself. This process is called impingement. It involves the removal of loosely adhered corroded surface layers on the metal or alloy by the high wall shear stress created by the flowing fluid. Examples of such erosion occur either where fluid is forced to turn direction, for example, at pipe bends or where high surface shear stresses can exist, for example on ship hulls.

Forms of Corrosion

The forms of corrosive attack that the most affect stainless steels include:

- general (uniform) corrosion;
- galvanic corrosion;
- pitting corrosion;
- crevice corrosion;
- intergranular corrosion;
- stress-corrosion cracking;
- high temperature corrosion.

General corrosion refers to corrosion dominated by uniform thinning that proceeds without localized attack. Weathering steels and copper alloys are good examples of materials that typically exhibit general attack, while passive materials, like stainless steels, are generally subject to localized attack. Under specific conditions, stainless steels are also susceptible to general corrosion. General corrosion is less deleterious than localized corrosion.

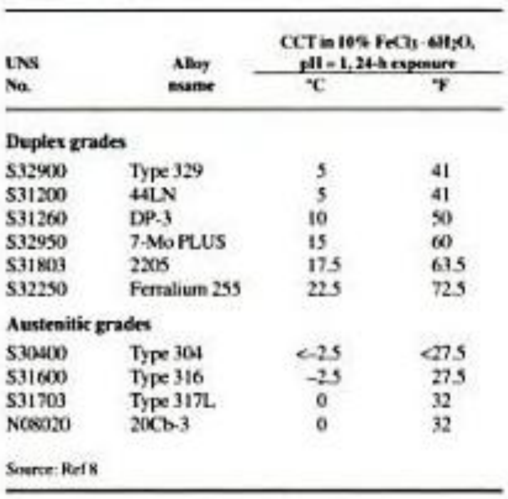
Galvanic corrosion results when two dissimilar metals are in electrical contact in a corrosive medium. As a high corrosion resistant metal, stainless steel can act as a cathode when in contact with a less noble metal, such as carbon or low alloyed steel.

The corrosion of carbon steel parts – for example, in stainless steel construction can be a significant problem.

Galvanic corrosion in stainless steel is difficult to predict because of influence of passivity. In the common galvanic series, a noble position is assumed by stainless steels in the passive state, while, a more active position is assumed in the active state. This dual position in galvanic series in chloride-bearing aqueous environment was the cause of many design errors. More precise information can be obtained using polarization curves, critical potentials and the mixed potential of galvanic couple.

Crevice corrosion can be considered a severe form of pitting. Any crevice whether the result of a metal to metal joint, a gasket, fouling or deposits, tend to restrict oxygen access, resulting in attack. Higher chromium and higher molybdenum grades are more resistant to crevice attack. For any metal there is a critical crevice temperature and it is important to know it for a correct material selection. Table 16 lists values for this critical temperature for some stainless steels.

Table 16 Comparison of critical crevice temperature (CCT) for duplex and austenitic stainless steels



UNS No.	Alloy name	CCT in 10% $FeCl_3 \cdot 6H_2O$, pH = 1, 24-h exposure	
		°C	°F
Duplex grades			
S32900	Type 329	5	41
S31200	44LN	5	41
S31260	DP-3	10	50
S32950	7-Mo PLUS	15	60
S31803	2205	17.5	63.5
S32250	Ferralium 255	22.5	72.5
Austenitic grades			
S30400	Type 304	<–2.5	<27.5
S31600	Type 316	–2.5	27.5
S31703	Type 317L	0	32
N08020	20Cb-3	0	32

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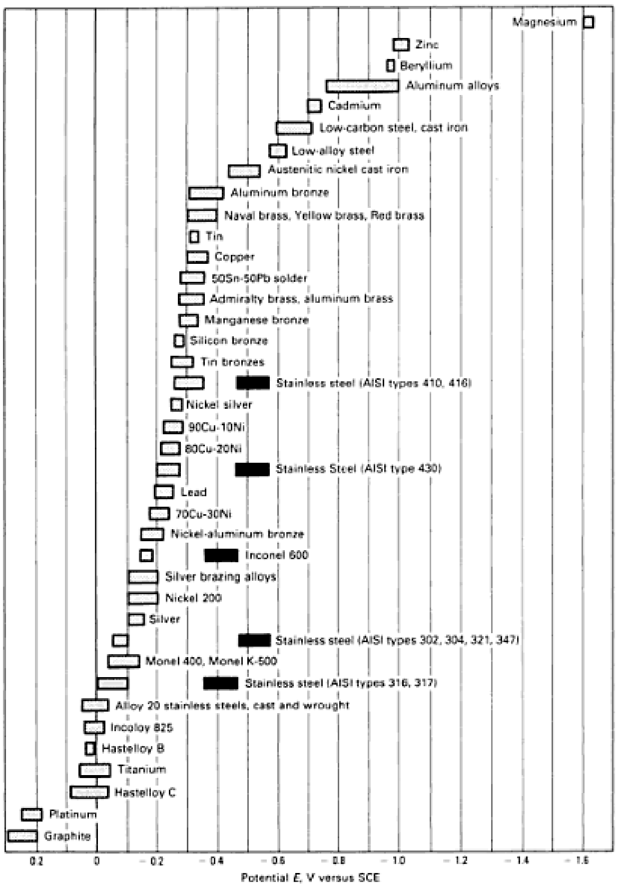


Fig.26 Corrosion potentials of various metals and alloys in flowing seawater at 10 to 25 gr.C. Flow rate was 2,4-4 m/s. Alloys are listed in order of the potential versus a saturated calomel electrode (SCE) in low velocity or poorly aerated water

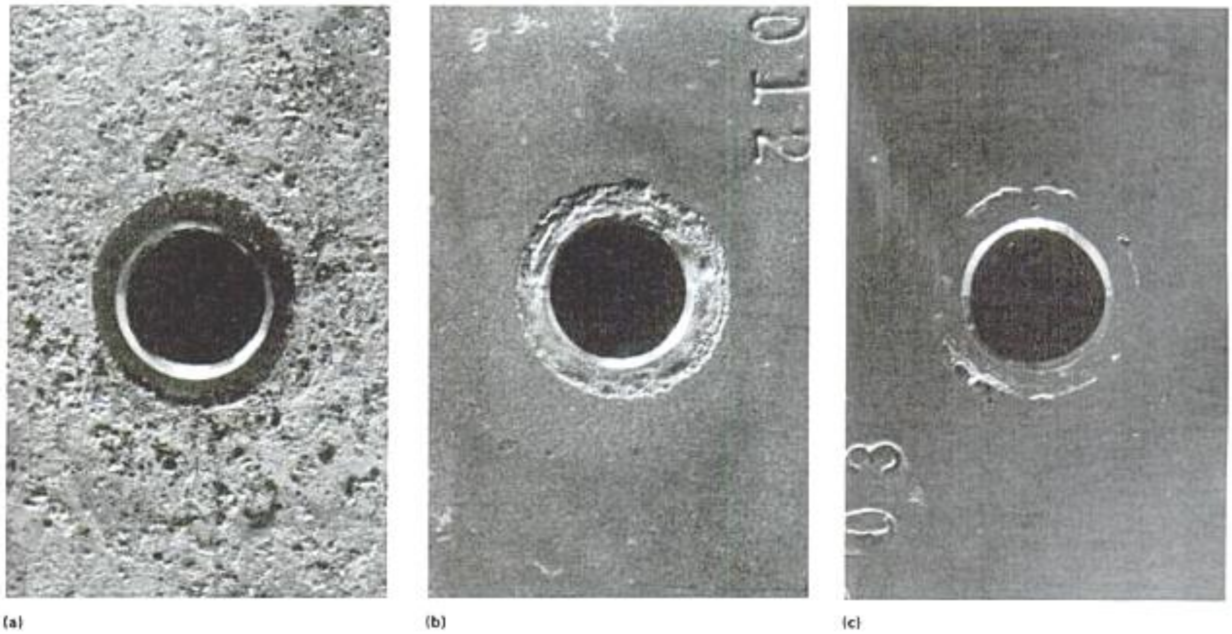


Fig. 27 Variation in stainless steels corrosion resistance in model SO_2 scrubber environment: (a)-304 steel in acid condensate; (b)-316 in acid condensate; (c)-304 in lime-stone slurry zone

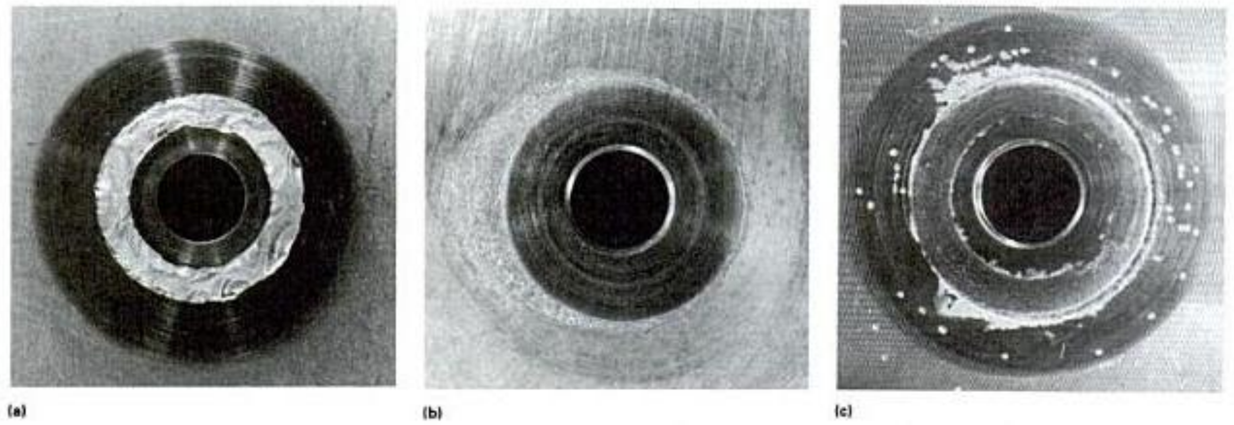


Fig. 28 Crevice corrosion on different alloys in natural seawater: (a)-904L stainless steel after 30 days; (b) 70Cu-30Ni alloy after 180 days; (c)-70Ni-30Cu alloy after 45 days

Intergranular corrosion. As we mentioned earlier in this work, intergranular corrosion is a permanent risk for stainless steels generally and for austentic steels – particularly.

If the austenitic stainless steels are cooled rapidly to below approximately 425 °C (800 °F), the carbides do not precipitate, and the steels are immune to intergranular corrosion. Reheating the alloys to 425 to 815 °C (800 to 1500 °F), as for stress relief, causes carbide precipitation and sensitivity to intergranular corrosion. The maximum rate of carbide precipitation occurs at approximately 675 °C (1250 °F). Because this is a common temperature for the stress relief of carbon and low-alloy steels, care must be exercised in selecting stainless steels to be used in dissimilar-metal joints that are to be stress relieved. Welding is the common cause of the sensitization of stainless steels to intergranular corrosion. Although the cooling rates in the weld itself and the base metal immediately adjacent to it are sufficiently high to avoid carbide precipitation, the weld thermal cycle brings part of the heat- affected zone (HAZ) into the precipitation.

Avoiding Intergranular Corrosion. Susceptibility to intergranular corrosion in austenitic stainless steels can be avoided by limiting their carbon contents or by adding elements whose carbides are more stable than those of chromium. For most austenitic stainless steels, restricting their carbon contents to 0.03% or less prevents sensitization during welding and most heat treatment. This method is not effective for eliminating sensitization that would result from long- term service exposure at 425 to 815 °C (800 to 1500 °F). At temperatures above 815 °C (1500 °F), titanium and niobium form more stable carbides than chromium and are added to stainless steels to form these stable carbides, which remove carbon from solid solution and prevent precipitation of chromium carbides. The most common of these stabilized grades are types 321 and 347. Type 321 contains minimum titanium content of 5 × (C% + N%), and type 347 a minimum niobium content of 8 ×C%. Nitrogen must be considered when titanium is used as a stabilizer, not because the precipitation of chromium nitride is a problem in austenitic steels, but because titanium nitride is very stable. Titanium combines with any available nitrogen; therefore, this reaction must be considered when determining the total amount of titanium required to combine with the carbon. The stabilized grades are more resistant to sensitization by long-term exposure at 425 to 815 °C (800 to 1500 °F) than the low-carbon grades are, and the stabilized grades are the preferred materials when service involves exposure at these temperatures. For maximum resistance to intergranular corrosion, these grades are given a stabilizing heat treatment at approximately 900 °C (1650 °F). The purpose of the treatment is to remove carbon from solution at temperatures where titanium and niobium carbides are stable, but chromium carbides are not. Such treatments prevent the formation of chromium carbide when the steel is exposed to lower temperatures.

Effect of Sigma Phase. The effect of σ phase on the corrosion behavior of austenitic stainless steel has received considerable attention. This hard, brittle intermetallic phase precipitates in the same temperature range as chromium carbide and may produce susceptibility to intergranular corrosion in some environments. Because it is hard and brittle, σ phase affects mechanical as well as corrosion properties. Although it is often associated with δ-ferrite, it can form directly from austenite. The effects of σ phase on the corrosion behavior of austenitic stainless steels are most serious in highly oxidizing environments. With standard grades such as 316L and CF3M, the problem is of practical concern only if the phase is continuous. Although discrete particles of σ phase may be attacked directly, such corrosion does not seem to contribute significantly to the penetration of the steel. With the more highly alloyed stainless steel grades, the precipitation of σ phase can result in a substantial loss in pitting and crevice corrosion resistance.

The most important corrosion problem with σ phase in austenitic stainless steels occurs before it is microscopically resolved . When the low-carbon molybdenum-containing austenitic stainless steels (such as type 316L and CF3M) or the stabilized grades (such as type 321 and type 347) are exposed at 675 °C (1245 °F), they may become susceptible to intergranular corrosion in nitric acid (HNO3) and, in some cases, Fe2(SO4)3-H2SO4. This susceptibility cannot be explained by carbide precipitation, and σ phase usually cannot be found in the optical microstructure. However, because some of the susceptible steels do exhibit continuous networks of σ phase, it has been assumed that this constituent is the cause of the intergranular corrosion. The hypothesis is that even when σ phase is not visible in the optical microstructure, its effects are felt through some precursor or invisible phase. Invisible σ phase must be considered when testing for susceptibility to intergranular corrosion, but it seems to affect corrosion resistance only in very oxidizing environments, such as HNO3.

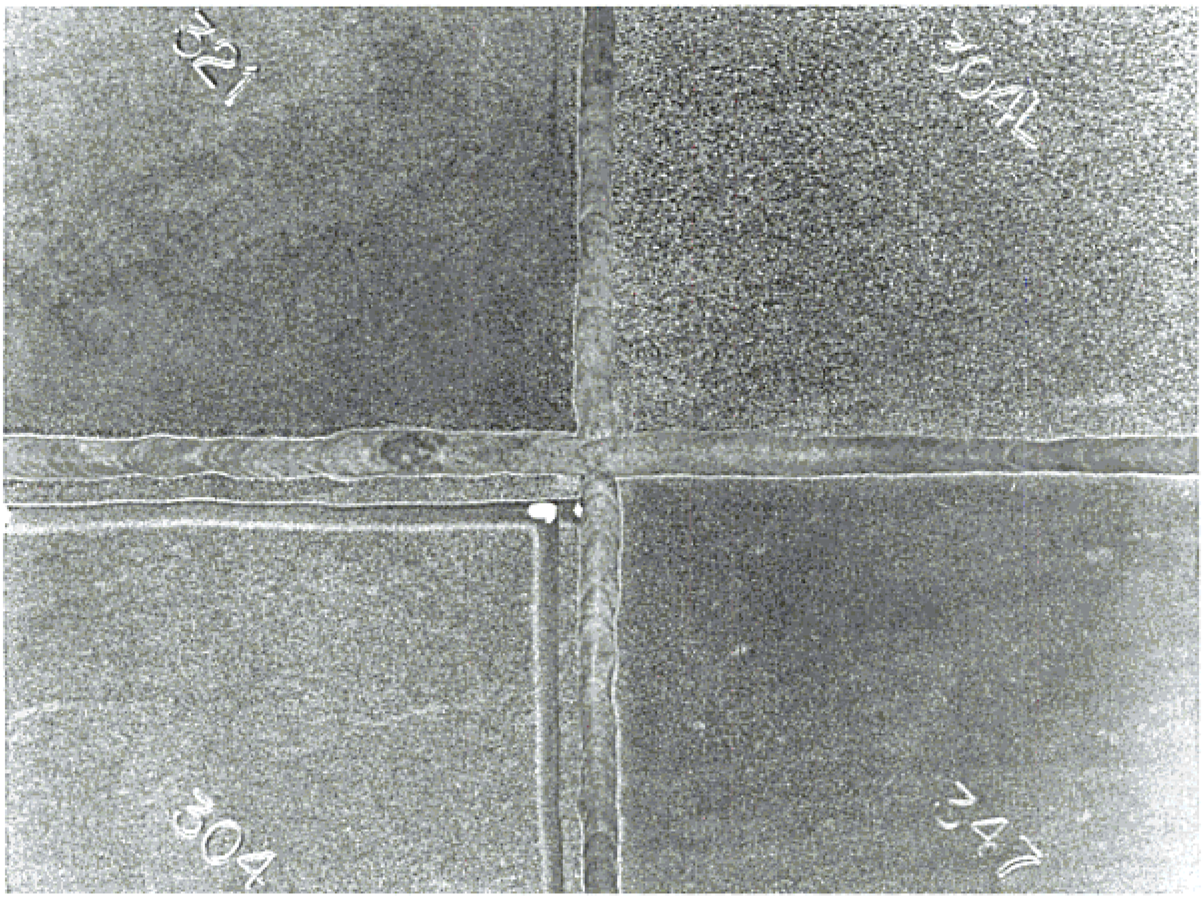
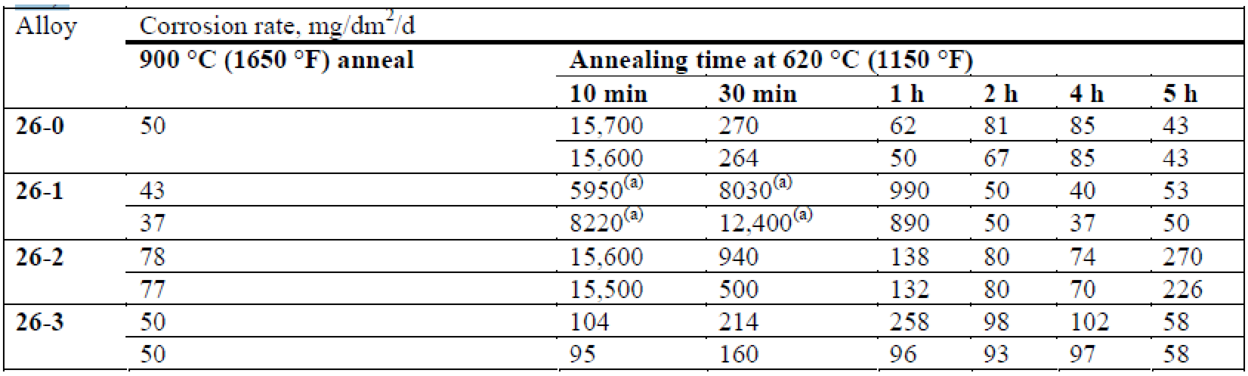


Fig. 29 Weld decay sensitization in austenitic stainless steels and methods for its prevention. Panels of four different 300 series were joined by welding and exposed to HNo3_Hf solution. The weld decay evident in 304 panel was prevented in the other panels by reduction of carbon content (304L) or by the addition of carbide stabilizing elements in type 321 and 347

In **ferritic** stainless steels, intergranular corrosion occurs in the same manner as for austenitic stainless steels but the conditions for precipitation of secondary phases along grain boundery are diferent. For example, the effects of annealing at 620 °C on the intergranular corrosion of 26% Cr alloys with 0 to 3% Mo were studied. The alloys contained 0.007 to 0.013% C and 0.020 to 0.024% N. As little as 10 min at temperature can lead to intergranular corrosion; however, continuing the treatment for 1 to 2 h can cure the damage (Table17). Increasing the molybdenum content delays the onset of sensitization and makes it less severe.



Alloy	Corrosion rate, mg/dm^2/d						
	900 °C (1650 °F) anneal	**Annealing time at 620 °C (1150 °F)**					
		10 min	**30 min**	**1 h**	**2 h**	**4 h**	**5 h**
26-0	50	15,700	270	62	81	85	43
		15,600	264	50	67	85	43
26-1	43	5950(a)	8030(a)	990	50	40	53
	37	8220(a)	12,400(a)	890	50	37	50
26-2	78	15,600	940	138	80	74	270
	77	15,500	500	132	80	70	226
26-3	50	104	214	258	98	102	58
	50	95	160	96	93	97	58

Table17 Corrosion rates of 26% Cr ferritic stainless steels containing 0 to 3% Mo that were annealed for 15 min at 900 °C (1650 °F), water quenched, annealed for increasing times at 620 °C (1150 °F), then water quenched

Testing was performed according to recommendations in ASTM A 763, practice X (ferric sulfate/sulfuric acid test).

(a) 56 h in test solution

Pitting corrosion.

Classical pitting corrosion caused by passive film breakdown will only occur in the presence of aggressive anionic species, and chloride ions are usually, although not always, the cause. The severity of pitting tends to vary with the logarithm of the bulk chloride concentration. The reason for the aggressiveness of chloride has been pondered for some time, and a number of notions have been put forth. Chloride is an anion of a strong acid, and many metal cations exhibit considerable solubility in chloride solutions. Chloride is a relatively small anion with a high diffusivity; it interferes with passivation, and it is ubiquitous as a contaminant.

The presence of oxidizing agents in a chloride-containing environment is usually extremely detrimental and will further enhance localized corrosion. It should be noted that chromate is an oxidizing agent that typically inhibits corrosion by reducing to form Cr ^{III}

film. Most oxidizing agents enhance the likelihood of pitting corrosion by providing extra cathodic reactants and increasing the local potential. Of course, dissolved oxygen is the most common oxidizing agent.

Electrochemical studies of pitting corrosion have found that characteristic potentials exist. Stable pits form at potentials noble to the pitting potential, *E*P, and will grow at potentials noble to the repassivation potential, *E*R, which is lower than *E*P. The effect of potential on pitting corrosion and the meaning of these characteristic potentials can best be understood with the schematic polarization curve shown in Fig.30. This figure is a plot of the potential versus the logarithm of the current density. Potential is measured versus a reference electrode, commonly a saturated calomel electrode (SCE), and a potentiostat is used, along with an auxiliary or counter electrode, to make such measurements. As mentioned previously, current density is a measure of the rate of reaction. Common practice for measuring such curves involves potentiodynamic polarization or automatic scanning of the potential from a low value, such as the corrosion potential, to higher values.

Alloy composition and microstructure can have strong effects on the tendency for an alloy to pit. Chromium concentration plays the dominant role in conferring passivity to ferrous alloys. The pitting potential was correspondingly found to increase dramatically as the chromium content increased above the critical 13% value needed to create stainless steel. Increasing the concentration of nickel, which stabilizes the austenitic phase, moderately improves the pitting resistance of iron-chromium. Small increases in certain minor alloying elements, such as molybdenum in stainless steels, can greatly reduce pitting susceptibility. Molybdenum is particularly effective but only in the presence of chromium. Small amounts of other elements, such as nitrogen and tungsten, also have a strong influence on the pitting resistance of stainless steels.

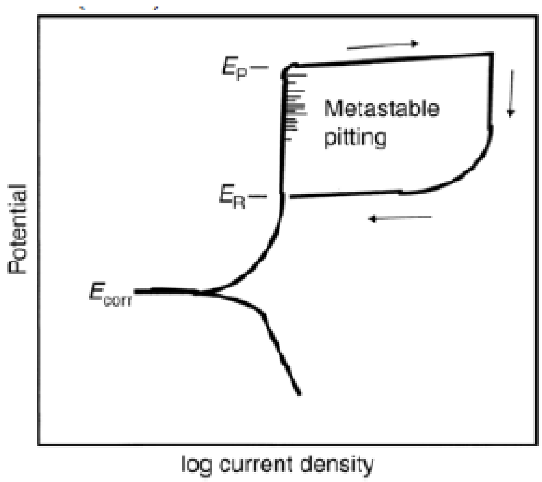


Fig. 30. Schematic of a polarization curve showing critical potentials and metastable pitting region. *E*P, pitting potential; *E*R, repassivation potential; *E*corr, corrosion potential.

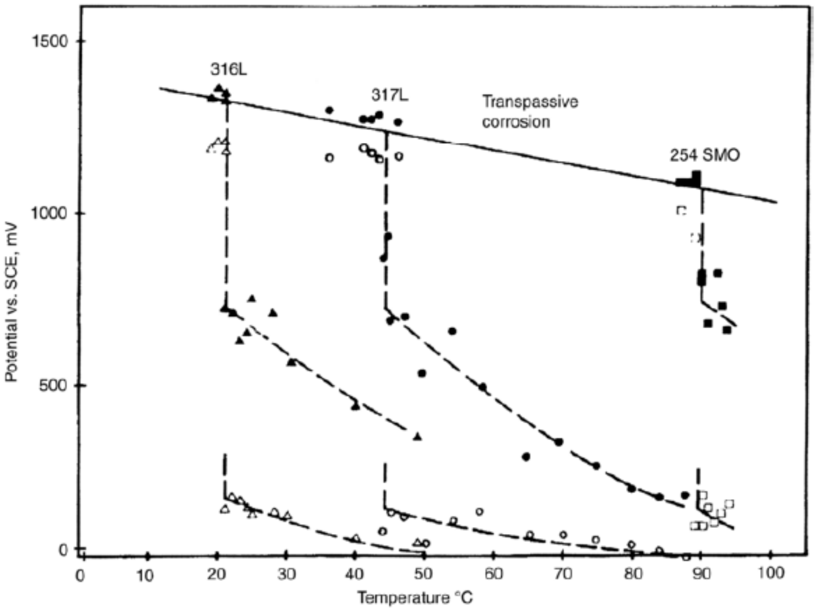


Fig.31 Pitting (filled symbols) and repassivation (open symbols) in 1 *M* NaCl as a function of temperature for different grades of stainless steel. SCE- saturated calomel electrode

Various measures have been developed to describe the beneficial effects of steel composition on resistance to localized corrosion. The pitting resistance equivalent number (PREN) was originally developed as a pitting index for stainless steels/1/:

PREN = Cr + 3.3Mo + 16N (wt%)

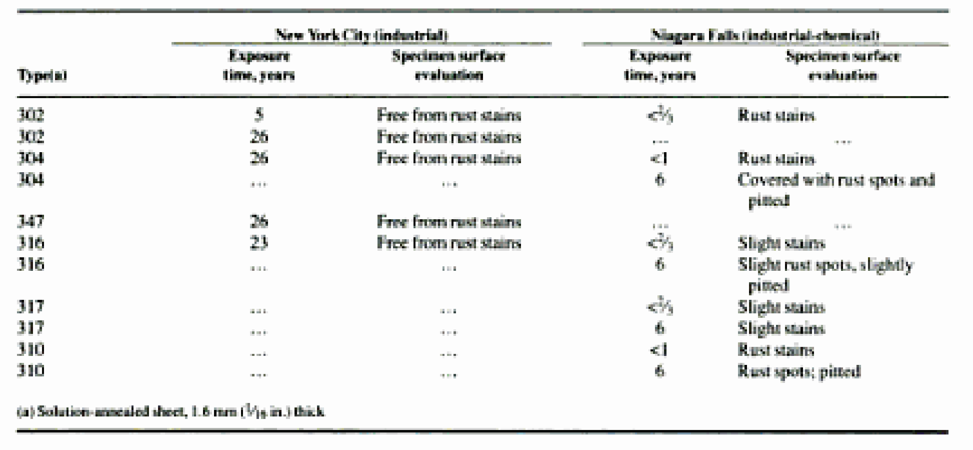
The multiplier value for nitrogen could be as high as 30.

Atmospheric Corrosion

The atmospheric contaminants most often responsible for the rusting of structural stainless steels are chlorides and metallic iron dust. The corrosivity of different atmospheric exposures can vary greatly and can dictate application of different grades of stainless steels. Rural atmospheres, uncontaminated by the industrial fumes or coastal salts, are extremely mild in terms of corrosivity for stainless steel, even in areas with high humidity. Industrial or marine environment can be considerable more severe. Tables 18 demonstrate that resistance to staining can depend on the specific exposure. For examples, several 300 series stainless steels showed no rust during long time exposure in New York City. On the other hand, staining was observed at Niagara Falls in a severe industrial-chemical environment near plants producing chlorine or HCl.

Stainless steels provide good resistance in marine atmospheres. Table 19 compares several 300 series stainless steels after 15 years exposure to marine atmosphere, at 250 m distance from the beach.

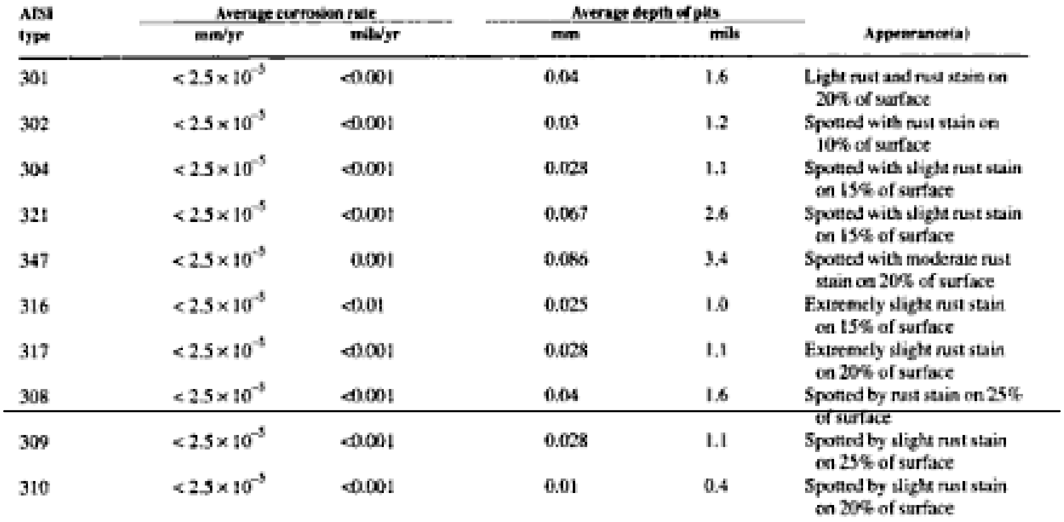
Table 18. Atmospheric corrosion of stainless steels at two industrial sites



Type(a)	New York City (industrial) Exposure time, years	New York City (industrial) Specimen surface evaluation	Niagara Falls (industrial-chemical) Exposure time, years	Niagara Falls (industrial-chemical) Specimen surface evaluation
302	5	Free from rust stains	$<\frac{2}{3}$	Rust stains
302	26	Free from rust stains	...	...
304	26	Free from rust stains	<1	Rust stains
304	...	...	6	Covered with rust spots and pitted
347	26	Free from rust stains	...	...
316	23	Free from rust stains	$<\frac{2}{3}$	Slight stains
316	...	...	6	Slight rust spots, slightly pitted
317	...	...	$<\frac{2}{3}$	Slight stains
317	...	...	6	Slight stains
310	...	...	<1	Rust stains
310	...	...	6	Rust spots; pitted

(a) Solution-annealed sheet, 1.6 mm ($\frac{1}{16}$ in.) thick

Table 19 Corrosion of 300 series stainless steels in marine atmosphere



AISI type	Average corrosion rate mm/yr	Average corrosion rate mils/yr	Average depth of pits mm	Average depth of pits mils	Appearance(a)
301	$< 2.5 \times 10^{-5}$	<0.001	0.04	1.6	Light rust and rust stain on 20% of surface
302	$< 2.5 \times 10^{-5}$	<0.001	0.03	1.2	Spotted with rust stain on 10% of surface
304	$< 2.5 \times 10^{-5}$	<0.001	0.028	1.1	Spotted with slight rust stain on 15% of surface
321	$< 2.5 \times 10^{-5}$	<0.001	0.067	2.6	Spotted with slight rust stain on 15% of surface
347	$< 2.5 \times 10^{-5}$	0.001	0.086	3.4	Spotted with moderate rust stain on 20% of surface
316	$< 2.5 \times 10^{-5}$	<0.01	0.025	1.0	Extremely slight rust stain on 15% of surface
317	$< 2.5 \times 10^{-5}$	<0.001	0.028	1.1	Extremely slight rust stain on 20% of surface
308	$< 2.5 \times 10^{-5}$	<0.001	0.04	1.6	Spotted by rust stain on 25% of surface
309	$< 2.5 \times 10^{-5}$	<0.001	0.028	1.1	Spotted by slight rust stain on 25% of surface
310	$< 2.5 \times 10^{-5}$	<0.001	0.01	0.4	Spotted by slight rust stain on 20% of surface

Corrosion in Waters

Waters may vary from extremely pure to chemically treated water to highly concentrated chloride solutions, such as brackish water or sea water, further concentrated by recycling. These chlorides content poses the danger of pitting or crevice attack of stainless steels. It is useful to consider two levels of chloride content: fresh water, containing up to 600 ppm chloride and seawater the contain brackish and severely contaminated waters.

In fresh water, 304 and 316 steels has provided excellent service but in seawater the risk of pitting and crevice corrosion exists if the flow rate decreases below about 1,5 m/sec.

Corrosion of Stainless Steels in Petroleum Products

The chemical composition of petroleum is highly complex. Petroleum is formed by various hydrocarbons present both in liquid phase (crude oil) and in form of gas, from which are extracted innumerous products: lubricant oil, LPG, gasoline, diesel, kerosene, and a large number of other products that are used as raw material in the petrochemical industry. However, it also presents many others chemical elements in its constitution, such as oxygen, nitrogen, sulfur, heavy metals, chloride, potassium and sodium. These elements may sometimes be considered impurities, being present in the form of sulfurated organic, nitrogenized, oxygenized, and organometalic compounds. Water, mineral salt, and sand are also impurities.

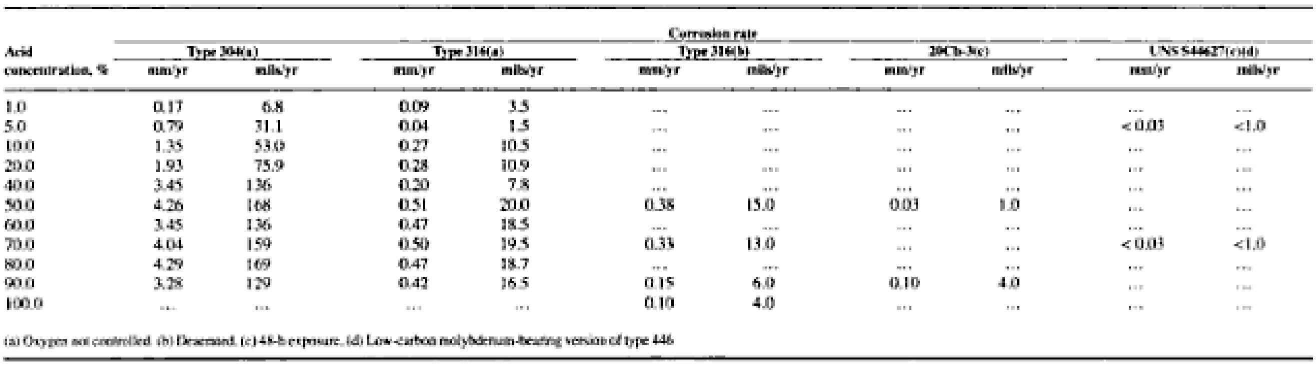
These impurities can give petroleum a high level of corrosiveness, depending on their concentrations/12/. For this reason, the steel used in the manufacturing of equipment to be used in the contact to petroleum products is usually covered with material highly resistant to corrosion. The appropriate selection of materials used in processing or manipulating petroleum products - is of the great importance, not only to guarantee the good functioning of the equipment and the necessary safety to the process, but also to reduce the costs involved. Therefore, the stainless steel is an important class of material used in the manufacturing of components, as well as in coating, since they present an excellent combination of mechanical properties and corrosion resistance.

The idea that petroleum hydrocarbons protect the surfaces of the pipes and the equipments that produce and process petroleum against corrosion is well accepted since a way of protecting metals against corrosion is apply oil and its derivative products (paints and varnish, forming a type of protective layer) on the surface of the pieces and equipment. However, when we refer to the crude oil, this protection is not effective due to the presence of the impurities previously mentioned. As we mentioned before in this work, there are three primary corrosive substances in the production of oil and gas: hydrogen sulfide (H2S), carbon dioxide (CO2), and dissolved oxygen (O2). These substances when in contact with the surfaces of the materials may initiate a process of corrosion that, either isolated or associated with other factors such as temperature, erosion due to fluid flow, and mechanical efforts, may cause failure in the components or equipments. **Even in the present work we can not consider the service condition as severe like in production of petroleum products – the effect of these corrosive agents can not be ignored.**

Recent works , conducted using mixtures of light petroleum distillates (naphtha and gasoline) with water content < 5 vol%, and in some cases with 10 ppm sodium chloride (NaCl) solutions, confirmed the electrochemical origin of the corrosion mechanism and showed that the main cause of corrosion in the petroleum distillates-electrolyte mixtures was the presence of water and dissolved oxygen. Critical water contents were obtained for naphtha-water and gasoline-water mixtures. Salts (chlorides, sulfates, and nitrates) and organic acids (formic [HCOOH] and acetic [CH_3COOH]) were extracted from the naphtha and gasoline by the aqueous phase and were responsible for the severe corrosion of these petroleum distillates. Valuable data regarding different types of corrosion attack (pitting or uniform corrosion) on mild steel were acquired during the study.

Chlorine dissolved in water forms a mixture of HCl and hypochlorous acid (HClO). The latter is very oxidizing and makes the mixture very corrosive. Following tables show the corrosion rate of several materials in saturated water-chlorine mixture.

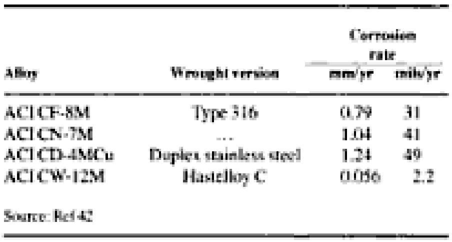
Table 20 Corrosion of Stainless Steels in HCOOH



Acid concentration, %	Corrosion rate									
	Type 304(a)		Type 316(a)		Type 316(b)		20Cb-3(c)		UNS S44627(c)(d)	
	mm/yr	mils/yr	mm/yr	mils/yr	mm/yr	mils/yr	mm/yr	mils/yr	mm/yr	mils/yr
1.0	0.17	6.8	0.09	3.5	...	...	...	...	...	...
5.0	0.79	31.1	0.04	1.5	...	...	...	...	< 0.03	<1.0
10.0	1.35	53.0	0.27	10.5	...	...	...	...	...	...
20.0	1.93	75.9	0.28	10.9	...	...	...	...	...	...
40.0	3.45	136	0.20	7.8	...	...	...	...	...	...
50.0	4.26	168	0.51	20.0	0.38	15.0	0.03	1.0	...	...
60.0	3.45	136	0.47	18.5	...	...	...	...	...	...
70.0	4.04	159	0.50	19.5	0.33	13.0	...	...	< 0.03	<1.0
80.0	4.29	169	0.47	18.7	...	...	...	...	...	...
90.0	3.28	129	0.42	16.5	0.15	6.0	0.10	4.0	...	...
100.0	...	...	...	...	0.10	4.0	...	...	...	...

(a) Oxygen not controlled. (b) Deaerated. (c) 48-h exposure. (d) Low-carbon molybdenum-bearing version of type 446

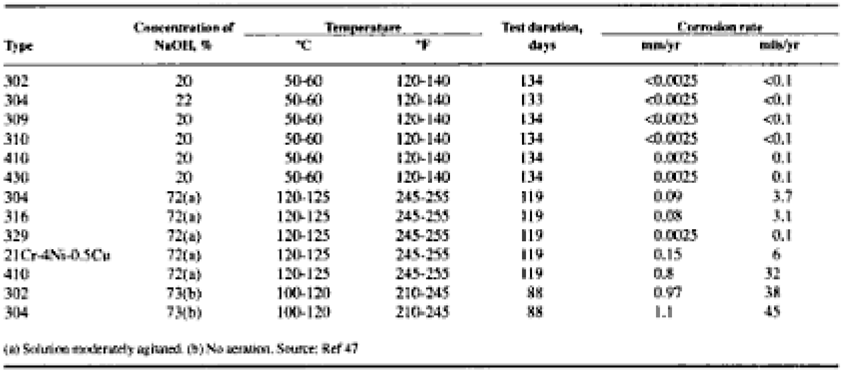
Table 21 Corrosion rate in chlorine-water for several materials



Alloy	Wrought version	Corrosion rate	
		mm/yr	mils/yr
ACI CF-8M	Type 316	0.79	31
ACI CN-7M	...	1.04	41
ACI CD-4MCu	Duplex stainless steel	1.24	49
ACI CW-12M	Hastelloy C	0.056	2.2

Source: Ref 42

Table 22 Corrosion data for stainless steels in NaOh solutions



Type	Concentration of NaOH, %	Temperature		Test duration, days	Corrosion rate	
		°C	°F		mm/yr	mils/yr
302	20	50-60	120-140	134	<0.0025	<0.1
304	22	50-60	120-140	133	<0.0025	<0.1
309	20	50-60	120-140	134	<0.0025	<0.1
310	20	50-60	120-140	134	<0.0025	<0.1
410	20	50-60	120-140	134	0.0025	0.1
430	20	50-60	120-140	134	0.0025	0.1
304	72(a)	120-125	245-255	119	0.09	3.7
316	72(a)	120-125	245-255	119	0.08	3.1
329	72(a)	120-125	245-255	119	0.0025	0.1
21Cr-4Ni-0.5Cu	72(a)	120-125	245-255	119	0.15	6
410	72(a)	120-125	245-255	119	0.8	32
302	73(b)	100-120	210-245	88	0.97	38
304	73(b)	100-120	210-245	88	1.1	45

(a) Solution moderately agitated. (b) No aeration. Source: Ref 47

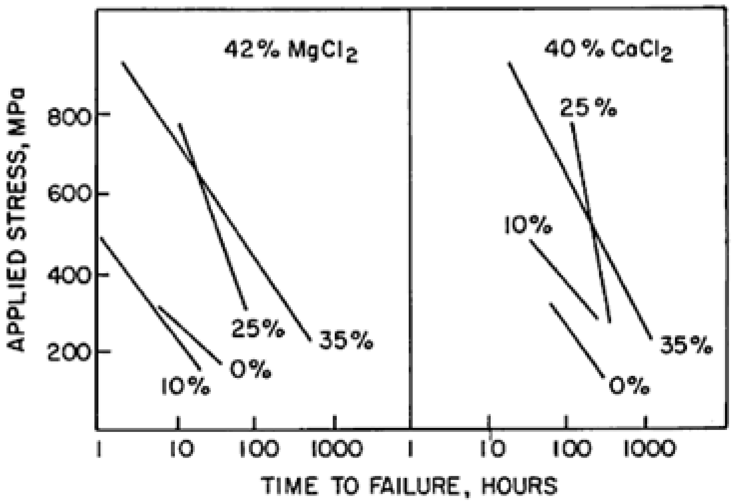
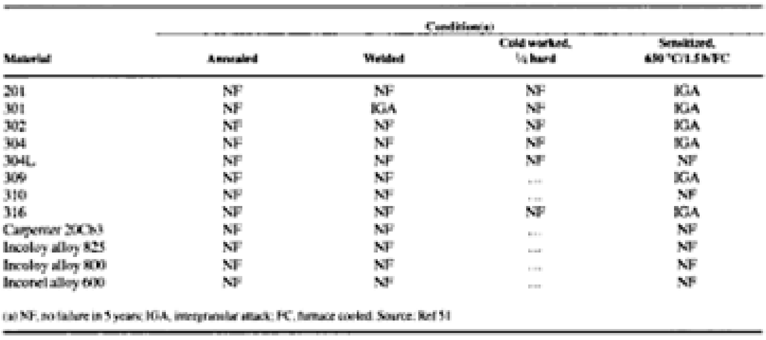


Fig. 32 Effect of cold-working (%) on the stress-corrosion cracking susceptibility of 321 grade stainless steel in boiling magnesium chloride and calcium chloride



Material	Condition(a)			
	Annealed	Welded	Cold worked, ½ hard	Sensitized, 650 °C/1.5 h/FC
201	NF	NF	NF	IGA
301	NF	IGA	NF	IGA
302	NF	NF	NF	IGA
304	NF	NF	NF	IGA
304L	NF	NF	NF	NF
309	NF	NF	...	IGA
310	NF	NF	...	NF
316	NF	NF	NF	IGA
Carpenter 20Cb3	NF	NF	...	NF
Incoloy alloy 825	NF	NF	...	NF
Incoloy alloy 800	NF	NF	...	NF
Inconel alloy 600	NF	NF	...	NF

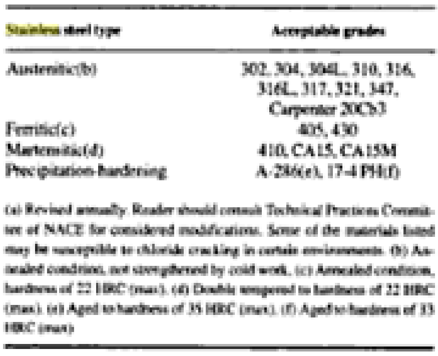
(a) NF, no failure in 5 years; IGA, intergranular attack; FC, furnace cooled. Source: Ref 51

Table 23. Results of SCC tests in which U-bend specimens were exposed for 5 years in wet marine atmosphere

Hydrogen Embrittlement

For SCC (Stress Corrosion Cracking) in aqueous environments, such as NaOH solutions, two mechanisms are discussed in the literature: SCC that is accelerated by the application of anodic currents and SCC that is accelerated by cathodic currents. Subsequent studies demonstrated that hydrogen enters steel when it is in contact with a neutral solution at both anodic and cathodic potentials. It is now widely accepted that in high strength stainless steel, hydrogen embrittlement is the crack propagation mechanism. In hardening precipitation stainless steels, this danger is obvious for yield stresses above 1035 MPa. That means that the heat treatment conditions are very important to minimize the risk of hydrogen embrittlement in this class of steels.

It is well known that the presence of Hydrogen sulphide in various environments decreases the hydrogen embrittlement resistance of the stainless steels.



Stainless steel type	Acceptable grades
Austenitic(b)	302, 304, 304L, 310, 316, 316L, 317, 321, 347, Carpenter 20Cb3
Ferritic(c)	405, 430
Martensitic(d)	410, CA15, CA15M
Precipitation-hardening	A-286(e), 17-4 PH(f)

(a) Revised annually. Reader should consult Technical Practices Committee of NACE for considered modifications. Some of the materials listed may be susceptible to chloride cracking in certain environments. (b) Annealed condition, not strengthened by cold work. (c) Annealed condition, hardness of 22 HRC (max). (d) Double tempered to hardness of 22 HRC (max). (e) Aged to hardness of 35 HRC (max). (f) Aged to hardness of 33 HRC (max)

Table 24 Stailess Steels listed in NACE Standard MR-01-75(a) as acceptable for sulphide environments

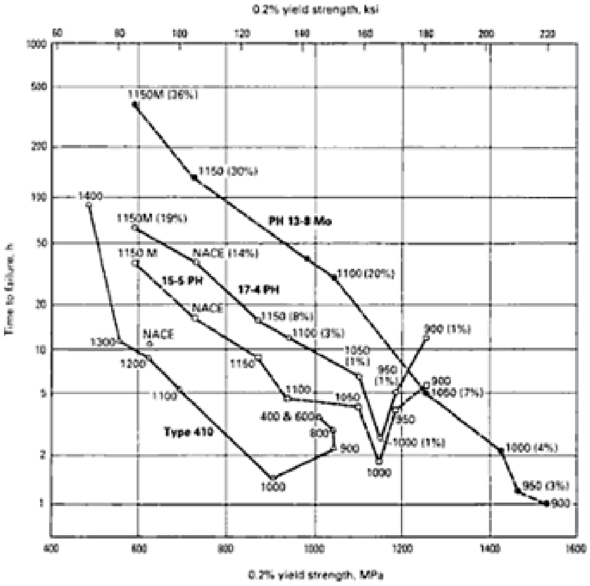


Fig. 33 Time to failure of various stainless steels as a function of yield strength when tested under 145 MPa in saturated hydrogen sulphide. Numbers adjacent to data points represent tempering or ageing treatments and parenthetical values are austenite percent in the microstructure

Erosion-Corrosion

Corrosion of a metal or alloy can be accelerated when there is an abrasive removal of the protective oxide layer. This form of attack is especially significant when the thickness of the oxide layer is an important factor in determining corrosion resistance. In the case of stainless steels, erosion of the passive film can lead to some acceleration of attack.

Material selection is an important consideration for erosion-corrosion resistance. Alloy hardness has also been shown to be a factor. Generally, soft alloys are more susceptible erosion-corrosion than their counterparts but the relative hardness properties of the alloy can be misleading because the hardening mechanism affects resistance to erosion-corrosion. For example, solution hardening has be found to offer greater resistance than that provided by conventional heat treatments.

As we mentioned before in this work, high values of hardness can be a deleterious factor in corrosion, especially in chloride environment. Even if erosion properties of the stainless steels require hard materials, we are going to find a balance between the two categories of properties. This balance will be reached by using hard particles deposition on the very active parts that work under erosion conditions.

3.2.4.5 Wear protection

To prevent premature wear of parts and components of the centrifugal separator in particular of scroll that causes the elimination of the solid phase, generally protects it with a layer of welded hard facing or spray coating with plasma jet.

For other components subject to wear as the exhaust nozzles of the fluids factions they will be replacing during exploitation.

In fig. 34 is shown surface protection areas of a centrifugal separator FLOTTWEG TRICANTER.

The significance of how to protect these surfaces shown in Fig. 34 are:

[1] Welded hard facing or spray coating;

[2] Ceramic;

[3] Tungsten carbide tiles,brazed or bolted;

[4] Chill casting;

[5] Plastic liners.

In order to minimaize maintenance costs for aplication involving abrasive products,all wear protection elements,except welded hard facing or spray coatings,are field-replaceable.

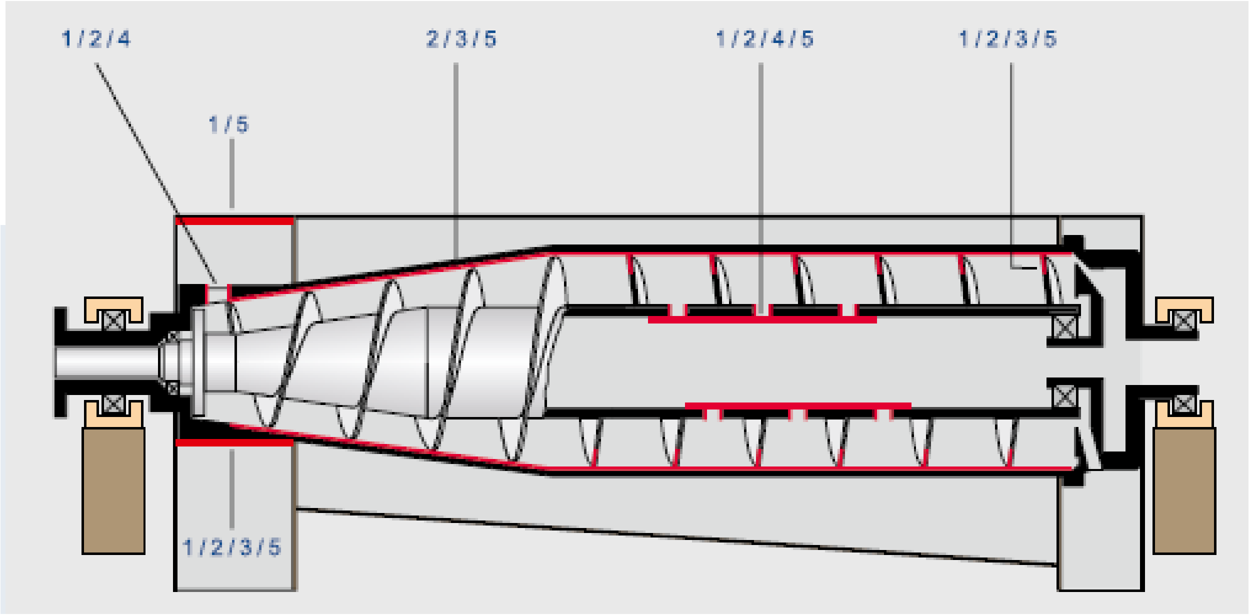


Fig.34 Surface protection areas of a centrifugal separator FLOTTWEG TRICANTER

3.3 The development of the final project theme

From operational schemes presented in fig. 5 and fig. 6 will define the main characteristics of an installation for recovery of oil spilled into the Danube.

3.3.1 The technical characteristics of the centrifugal separator

-**Axis position – orizontal**. This configuration has the advantage that both bearings separator and drive motors are not required to axial forces.
-Effectiveness factor z value will be around 3000. For this reason, it is necessary a scroll diameter of 350 mm for an estimated maximum speed of the compressor housing about 4000 rpm.
- Construction type of the separator: in counter-current. This configuration has the advantage of increased retaining time of the mixture into a separator, in order to assure an effective separation.
-Drive system. Drive systems of bowl and the scroll will be fitted with variable speed motors controlled with frequency converters to ensure optimal system programmed. Will be dimensioned the maximum necessary power for the aggregates. These powers should be provided in all the situations where the centrifugal separator is installed on the ship, on a ground vehicle or ground fixed.
- Conditions for moving parts. All moving parts are statically and dynamically balanced in class-G 2.5 according to ISO 1940 SREN.
-The quantity of wastewater processed. The feed rate must be about 15÷25 m^3/h. This is function of the mixture caracteristics.

3.3.2 The technical characteristics for other components

-**Protective barrier.** Water quality monitoring stations will be equipped with systems to prevent the spread of pollution upstream. Following studies, will be designed multilayer barrier to the spread of the upstream petroleum
-**The filtration and suction system.** The filtration system must be dimensioned in such a way to allow the crossing of designed flow in the quantity and quality needed for the suction pump to function. The suction pump must ensure the designed flow for the centrifugal installation with an adjustable output pressure of 4÷7 bar. When your

centrifuge plant is installed on a ground vehicle or fixed to the ground, it is necessary that the collection system to be mounted on a floating platform, remotely controlled.

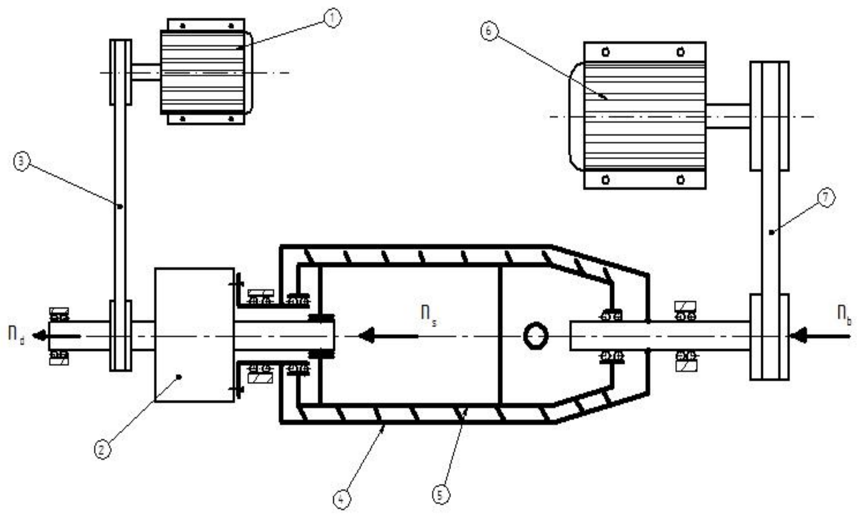
- **Sizing of storage elements** (storage tanks) of petroleum and solid fractions. For the operation on the ship and on the ground it is necessary to be sized the tanks for the recovery of oil and the solid fraction to ensure a continuous and as long as possible removement of the effects of pollution. Following the results presented in the chapter 3.4 solid concentration fractions in Danube waters generally do not exceed 4000 mg/l. After one hour of operation with a feed flow of 20 m^3, will result a solid fraction about 24 kg for a 40% water concentration in mixture.

3.3 The development of the final project theme

From operational schemes presented in fig. 5 and fig. 6 will define the main characteristics of an installation for recovery of oil spilled into the Danube.

3.3.1 The technical characteristics of the centrifugal separator

Following studies of centrifugal separators for to meet the requirements of this project (three phase separation) in fig.35 is presented general scheme proposed for the plant to be designed.



Note

1 Differential gear drive motor.
2. Differential gear.
3. Belt drive differential gear input shaft.
4. Bowl
5. Scroll anssy.
6. Drive motor centrifuge bowl.
7. Belt drive centrifuge bowl.

n_b -rotational bowl speed (rpm)
n_d -rotationall speed of diferential gear input shaft (rpm)
n_s -rotational scroll speed (rpm)

Fig. 35 General scheme of a centrifugal separator

-**Axis position –horizontally**. This configuration has the advantage that both bearings separator and drive motors are not required to axial forces.

-Effectiveness factor z or g force (maximum overload in the centrifugal separator) value will be around 3000. For this reason, it is necessary for a scroll diameter of 350 mm an estimated maximum speed of the compressor housing about 4000 rpm.

- Construction type of the separator: in counter-current. This configuration has the advantage of increased retaining time of the mixture into a separator, in order to assure an effective separation.

-Drive system. Drive systems of bowl and the scroll will be fitted with variable speed motors controlled with frequency converters to ensure optimal system programmed. Will be dimensioned the maximum necessary power for the aggregates. These powers should be provided in all the situations where the centrifugal separator is installed on the ship, on a ground vehicle or ground fixed.

To achieve the differential speed between the bowl and scroll separator is used differential gears. Obtaining a affordable Δn difference between bowl and the scroll speed is essential for proper processing of wastewater.

In Fig 36 is shown cinematic scheme of a differential gear reducer designed to provide a proper speed of a scroll separator.

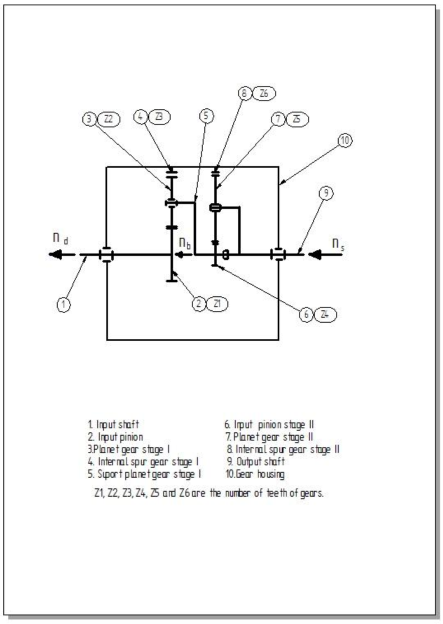


Fig.36 Cinematic scheme of a differential gear

The main feature is that the differential reduction gears are systems with two degrees of freedom, in this case are two-speed input and single output speed.

The two speeds of entry are: n_d ; rotationall speed of diferential gear input shaft and n_b rotationall speed of the bowl who is connected to the housing of differential reducer.

Nominal reduction ratio for a differential gear is:

$Z_n=(n_b-n_d)/(n_b-n_s)$ III

The difference (n_b-n_s) between the bowl and scroll speed correlated with the efficiency factor z is very important for optimal separation of polluted water.

If in the formula III bowl speed is equal to zero, then the internal transmission gear ratio for a differential reducer is:

$i_n=n_d/n_s=(z_6+z_4)(z_3+z_1)/(z_1*z_4)$ IV

By combining relations III and IV give a connection between input and output speeds necessary for programming the working regime of the centrifugal separator.

In recent years there has developed a new generation of reducers for centrifugal separators higher than conventional with spur gears. They are called cycloidal gear and has many advantages over the conventional gears.

In Fig. 37 is presented a section through a cycloidal reducer.

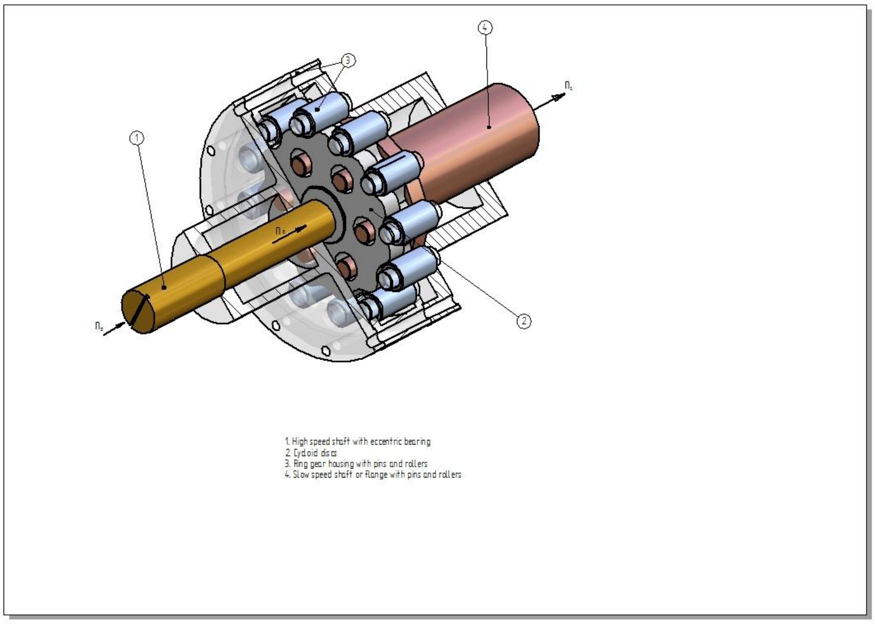


Fig. 37 Simplified section of a cycloidal reducer

The reduction ratio can be calculated from the following equation:

$$\mathbf{Z_n = -(n_b - n_d)/(n_b - n_s) \quad IIII}$$

- = Change of rotational direction between input and output

Internal transmission gear ratio of the cycloidal reducer is:

$i_n=(N-M)/M$ where:

N= the number of internal pins;

M= the number of cycloid disc teeth

Rotational speeds of formula IIII have the same meanings as in formula III

The operating principle of the cycloidal reducer

As the eccentric cam rotates, it rolls the cycloid discs around the internal circumference of the stationary ring gear. The resulting action is similar to that of a wheel rolling around the inside of a ring.

As the wheel (cycloid disc) travels in a clockwise path around the ring (ring gear housing), the wheel itself turns slowly on its own axis in a counter-clockwise direction.

In the CYCLO system the cycloidal profile around the outer edge of the disc engages progressively with the rollers of the fixed ring gear housing to produce a reverse rotation at reduced speed. For each complete revolution of the high speed shaft the cycloid disc turns one cycloidal tooth pitch inthe opposite direction.

In general, there is one less cycloidal tooth around the disc than there are pins in the fixed ring gear housing, which results in reduction ratios being numerically equal to the number of cycloidal teeth on the disc. (NOTE: On some ratios, there are two less teeth per cycloid disc than there are pins in the ring gear housing.)

The reduced rotation of the cycloid discs is transmitted to the slow speed shaft by means of drive pins and rollers which engage with holes located around the middle of each disc. The rotation of the cycloid discs is transmitted to the slow speed shaft via the pins and rollers projecting through holes in the cycloid discs.

Normally a two disc system is used with a double eccentric cam which increases the torque capacity and offers an exceptionally smooth vibration-free drive.

Features and Benefits of cycloidal geraring

- **500% Shock Overload Capacity**

Since the CYCLO system distributes the load to numerous cycloid teeth, it can withstand momentary intermittent shock overloads of up to 500% of the rated torque in extreme emergency situations.

Here’s why:

At least 30% of the CYCLO’s unique disc profiles share the shock overload and the components are in compression –so can’t be sheared off.

- **Compact Size**

Reduction ratios from 3:1 to 119:1 are available for single stage units and for example, triple stages units offer ratios up to almost 1,000,000:1.

- **Overall Economy**

Competitive initial cost, high reliability, long life and minimum of maintenance give CYCLO gearmotor superior overall economy when compared to conventional gearboxes.

- **Capacity for Frequent Start- Stop and Severe Reversing**

The inertia the CYCLO speed reducer is reduced to a minimum, so that it responds quickly in these applications.The shear-free cycloidal profile makes the unit ideal for those applications that quickly wear out competitor's reducers.

- **Low Noise**

When compared with the sliding tooth contact of conventional helical gears, the CYCLO system provides reduced noise level.

●High Efficiency even at High Ratios

Torque transmitting parts have a rolling action with minimal friction, so the overall efficiency is as high as 95% in single stage units.

- **No Thermal Factor Limitations**

CYCLO gearmotors and speed reducers smooth, almost frictionless operation all but eliminates the conventional limitations due to heat. In all sizes and combinations, the drive has a thermal rating that exceeds mechanical capacities.

- **Exceptional Life**

Tests on Cyclo units show negligible wear after 50,000 hours, and experience shows that future wear and tear is insignificant.

- Conditions for moving parts. All moving parts are statically and dynamically balanced in class-G 2.5 according to SR ISO1940-1:1994

-Conditions for bearings

Centrifugal separator plant will be equipped with ball or roller bearings. The lubrication for these components will be grease.

For differential gearbox lubrication system is oil by centrifugation. This closed lubrication system is effectively when power transmitted to drive the scroll is less than 50 KW.

-The quantity of wastewater processed. The feed rate must be about 15÷25 m^3/h. This is function of the mixture caracteristics.

3.3.2 The technical characteristics for other components

-Command and control system.

This should display the functional parameters of the plant (processing rate flow, rotational speed of moving parts, temperatures in the bearings) and stop the operation when critical values are exceeded. These values of critical functional parameters will be determineted in the next stage of the project.

- **Protective barrier.**

Water quality monitoring stations will be equipped with systems to prevent the spread of pollution upstream. Following studies, will be designed multilayer barrier to the spread of the upstream petroleum.

- **The filtration and suction system.**

The filtration system must be dimensioned in such a way to allow the crossing of designed flow in the quantity and quality needed for the suction pump to function. The suction pump must ensure the designed flow for the centrifugal installation with an adjustable output pressure of 4÷7 bar. When your centrifuge plant is installed on a ground vehicle or fixed to the ground, it is necessary that the collection system to be mounted on a floating platform, remotely controlled.

- **Sizing of storage elements** (storage tanks) of petroleum and solid fractions. For the operation on the ship and on the ground it is necessary to be sized the tanks for the recovery of oil and the solid fraction to ensure a continuous and as long as possible removement of the effects of pollution. Following the results presented in the chapter 3.4 solid concentration fractions in Danube waters generally do not exceed 4000 mg/l. After one hour of operation with a feed flow of 20 m^3, will result a solid fraction about 24 kg for a 40% water concentration in mixture.

3.4 CONCLUSIONS

In this stage the activities were dedicated to define of the final project theme.

It was necessary to develop research activities end to realize studies.

In chapter no. 3.1.:

- Were reviewed many construction possibilities and types of the separation the multiphase mixtures.
- Were defined two big solutions for the installation’s position: on the soil or on the water, with diverse other possibilities; mobile at soil or fix, etc.

In chapter no. 3.2.

- Were studied the technological implications related with the complex process of multiphase centrifugal separation:
- Study of the chemical composition and physical proprieties of the petroleum products which can become various pollutants;
- Study regarding the possible pollution degree with petroleum products;
- Research on the solids contained in the Danube water regarding the turbidity;
- Measurements and probes of the Danube water;
- The selection of the materials:
- Corrosion and fatigues. The analyze of the metallic materials’ proprieties possible used for the centrifuge’s construction.

In the chapter no. 3.3., based on these studies and researches regarding on a side the composition of the multiphase mixture and on another side of the technological possibilities to realize a separation installation by centrifugation, were defined the technical and functional characteristics of the multiphase separator. The separation installation is very complex equipment. The centrifuge represents “the heart”, being necessary other annex installations for the good development of the entire process.

After the project theme’s definition were realized the necessity to use some kind of protective barriers to avoid the pollution spreading on wide surfaces and uncontrollable and also the necessity to control and, after the processing, to storage the petroleum component and the solid component, the water being purged back to the Danube water.

The main parameters that we had in mind, considered representative to our study and to the project were: TPH, oils, fatties, pH, turbidity, transparency and sediments.

The first tests have been performed by Bulgarian specialists, in 10 locations along the Danube river, Bulgarian coast regions Ruse (6 locations) and Silistra (4 locations).

The tests have been performed by the Bulgarian specialists from Petrol – Control – Ltd, Water, Solvents and Petroleum Testing Laboratory from Ruse - Bulgaria, an accredited Laboratory in compliance with the European and Bulgarian State Standard EN ISO/IEC 17025:2006

TPH term express provisionally content in the water of a polar and weakly polar compounds extractable with hexane (or petroleum ether). To determine TPH, the following methods are used: weight, spectral and chromatographic. For lab tests, were used a gas-liquid chromatography method, with a gas chromatograph HP 5980.

pH is determined colorimetrically by buffering solutions or with potentciometric titration.

The first method does not require special equipment and is based on comparing the color of sample water added to it an appropriate indicator of the color buffer of known pH, containing the same amount of indicator. The method yielded precision of potentiometric one.

Potentiometric determination of pH with glass electrode is based on that the change of pH by one unit causes a potential change of the electrode with 58,1 mV at 20 C.° The dependence pH / potential of the electrode is linear over the range pH 1 to 11 and depends on the material of the glass electrode. Determination by this method do not interfere with color, turbidity, presence of oxidants in the sample, high content of salts and the presence of oil in it.

Analysis of the samples was carried out by this method on pH meter MV 88.

Both ***turbidity (transparency)*** indicators serve as an indirect assessment of the content of mechanical impurities in the water. In the content of suspended substances in water is determined to 3mg/dm3 transparency, and above this amount - water turbidity.

Reading to the measurement of turbidity is usually performed in photometric standard graph: concentration of SiO2 - light absorption, thus the lightoversigth of the sample compares to that of a standard suspension of SiO2 or kaolin.

In our conditions, turbidity was performed on Spectrophotometer Spekol 11 Carl Zeiss Jena, Germany, and type spectrophotometer DR 3800.

The ***sediments*** represent mechanical impurities in the water with different backgrounds - mineral, mineral-organic or organic.

The most reliable method for determining the quantity of sludge is filtering through a filter of appropriate porosity and weight determination of the amount of retained substances from the filter.

Indirectly (not exactly), but faster the sludge is carried out on turbidity indicator (transparency) of water.

Sediments of the samples from the Danube defined weighting method and indicator "turbidity”.

The test results are object to the protocols No.601 – 610 and the chemical characteristics obtained are presented in the following table 1:

Graphically representing the leading indicators (turbidity, sediments, pH, solids and oil), as function on which km were done the sampling, in the monitoring period (19.05.2011 – 28.05.2011), we found higher values of oil and solids concentration and proportion of sediments in the Russian region of km 485-488, region where the turbidity recorded the lowest values. pH values are normal ones, between 6,88 and 8,35.

These values are consistent with average values of TOC (Total organic carbon) and DOC (Disolved organic carbon) from the last official report TNMN - ICPDR (final version 2010).

The project will continue with monitoring of these indicators of the Danube River and in the same time with analyzing the possible pollutant petroleum fractions, in order to achieve a realistic design of the separation plant.

The separator that is subject of this project includes two category of parts, according the mechanical efforts and environmental conditions, in service. These are:

- components directly exposed to severe corrosive environment (water petroleum products mixtures, atmospheric corrosion), moderate mechanical efforts and erosion (sludge) conditions; it is important to note that petroleum products are not corrosive by them self but their impurities and water, containing other impurities, can be deleterious;
- parts that are not in direct contact to the water-petroleum mixture but are subjected to corrosion phenomena in atmospheric environment and moderate mechanical stresses.

The material selection for the first cathegory parts are very challanging. It is obvious from the data included in this study – which a stainless steel is necesary to avoid corrosion but the grade of stainless steel deserves an annalyse. Martensitic and hardening stainless steels are excluded by their poor behaviour in corrosive environment and by their high susceptibility to hydrogen embritlement and stress corrosion cracking. Even if they involve lower alloying levels and lower costs, asociated to high mechanical performances - the risk to use them is very high. Austenitic stainless steels exhibit a good corrosion resistance and stability in their mechanical response, in a wide range of temeperatures, from under zero to few hundred degrees.

The main problems of austenitic stainless steel are the susceptibility to intergranular corrosion in senzitivisation conditions and their reactivity against the chloride environment at high temperatures. Duplex (austenitic+ferritic) stainless steels are less sensitive to intergranular corrosion, are allmost immune to the chloride environment even at high temperatures and they exhibits mechanical characteristics about twice higher than austenitic steels.

The major disadvantage of duplex stainless steels is that they are very expensive because of their high nickel and chromium content.

Because high temperatures service is not a specific concern in this project we decide to choose an austenitic stainless steels, with a low carbon content to reduce the intergranular corrosion risk and a moderate molibdenum level, to prevent the pitting corrosion. **This is 316L grade austenitic stainless steel**.

For the very active areas of the parts, that work in erosion - corosion conditions, we propose to apply a hard-particles deposition (stellite or tungsten carbide).

The parts that are not in direct contact to the water + oil mixtures can be made from usual carbon or low alloyed steels, protected against the atmosphere corrosion by usual methods.

In order to create a common structure for checking and managing the Danube pollution, and in the same time to issue the purposed strategy in the frame of this project, Romanian and Bulgarian specialists and researchers have performed tests for evaluating the quality of Danube water. These joint technical efforts will help in protecting the environment and to find efficient solutions for cleaning the oil products from polluted water.

The realization of the stage 3 of the project allows us to declare that we made important steps in the implementation by determining the conditions under which works the proposed equipment and by defining project theme. Also it should be noted that the work of the team took place in the best conditions, the collaboration between project partners has been very good. The technical language used by a high scientific quality has overcome the language barrier between partners.

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Chapter VI.Field Methods For The Analysis Of Petroleum Hydrocarbons

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ANNEX

Protocol: Test 601/02.06.2011

Protocol: Test 602/02.06.2011

Protocol: Test 603/02.06.2011

Protocol: Test 604/02.06.2011

Protocol: Test 605/02.06.2011

Protocol: Test 606/02.06.2011

Protocol: Test 607/02.06.2011

Protocol: Test 608/03.06.2011

Protocol: Test 609/03.06.2011

Protocol: Test 610/03.06.2011

Testing the Danube river – Abstract and Conclusion

In order to create a common structure for checking and managing the Danube pollution, and in the same time to issue the purposed strategy in the frame of this project, Romanian and Bulgarian specialists and researchers have began to perform tests for evaluating the quality of Danube water. These joint technical efforts will help in protecting the environment and to find efficient solutions for cleaning the oil products from polluted water.

The main parameters that we had in mind, considered representative to our study and to the project were: TPH, oils, fatties, pH, turbidity, transparency and sediments.

The first tests have been performed by Bulgarian specialists, in 10 locations along the Danube river, Bulgarian coast regions Ruse (6 locations – Fig. 1) and Silistra (4 locations – Fig.2):

DANUBE RIVER - ROUSSE AREA
(505 км - 484 км)

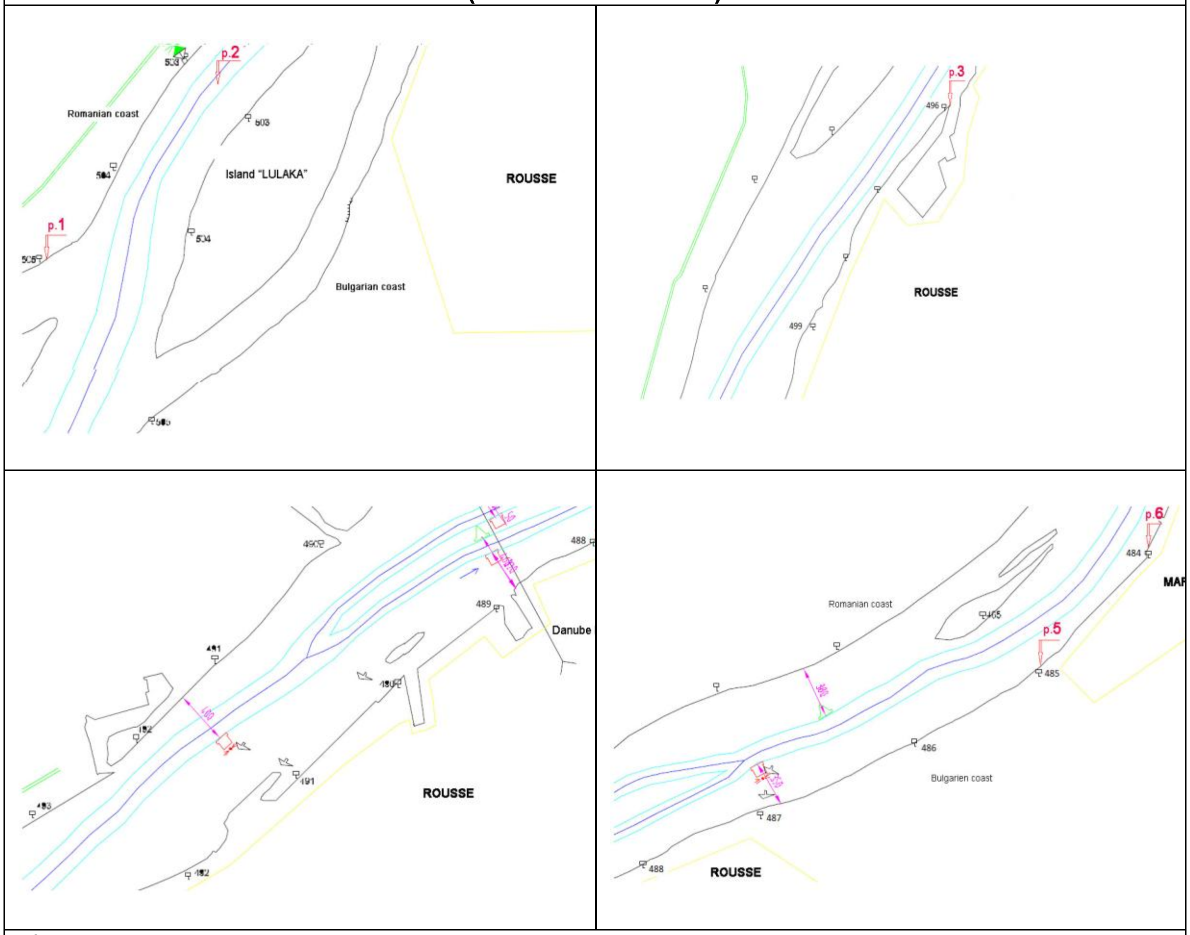


Fig. 1 **LEGEND:**

point 1 - **505 км** (Island “Liuliaka”) Romanian coast;
point 2 - **503 км** ((Island “Liuliaka”)) middle of the river;
point 3 **- 496 км** (Limana)) Bulgarian coast;
point 4 **- 488 km** Bulgarian coast
point 5 **- 485 km** (KTM) Bulgarian coast
point 6 **- 484 km** (Rompetrol) Bulgarian coast

DANUBE RIVER - SILISTRA AREA
(379 км - 374,5 км)

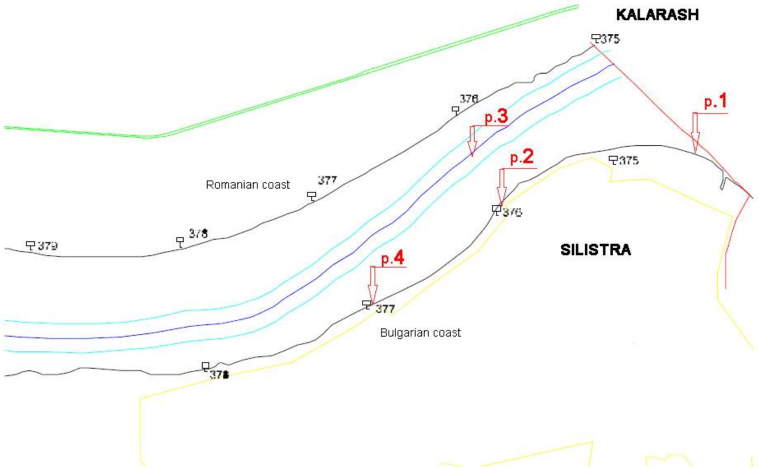


Fig. 2 **LEGEND:**

point 1 - **374,5 км** Bulgarian coast;
point 2 - **376 км** (hotel “DRASTAR”) Bulgarian coast ;
point 3 **- 376 км** (hotel “DRASTAR”) middle of the river (round fairway);
point 4 **- 377 km** (Danube park – west side) Bulgarian coast

The tests have been performed by the Bulgarian specialists from Petrol – Control – Ltd, Water, Solvents and Petroleum Testing Laboratory from Ruse - Bulgaria, an accredited Laboratory in compliance with the European and Bulgarian State Standard EN ISO/IEC 17025:2006

TPH term express provisionally content in the water of a polar and weakly polar compounds extractable with hexane (or petroleum ether). To determine TPH, the following methods are used: weight, spectral and chromatographic. For lab tests, were used a gas-liquid chromatography method, with a gas chromatograph HP 5980.

pH is determined colorimetrically by buffering solutions or with potentciometric titration.

The first method does not require special equipment and is based on comparing the color of sample water added to it an appropriate indicator of the color buffer of known pH, containing the same amount of indicator. The method yielded precision of potentiometric one.

Potentiometric determination of pH with glass electrode is based on that the change of pH by one unit causes a potential change of the electrode with 58,1 mV at 20 C.° The dependence pH / potential of the electrode is linear over the range pH 1 to 11 and depends on the material of the glass electrode. Determination by this method do not interfere with color, turbidity, presence of oxidants in the sample, high content of salts and the presence of oil in it.

Analysis of the samples was carried out by this method on pH meter MV 88.

Both ***turbidity (transparency)*** indicators serve as an indirect assessment of the content of mechanical impurities in the water. In the content of suspended substances in water is determined to 3mg/dm3 transparency, and above this amount - water turbidity.

Reading to the measurement of turbidity is usually performed in photometric standard graph: concentration of SiO2 - light absorption, thus the lightoversigth of the sample compares to that of a standard suspension of SiO2 or kaolin.

In our conditions, turbidity was performed on Spectrophotometer Spekol 11 Carl Zeiss Jena, Germany, and type spectrophotometer DR 3800.

The ***sediments*** represent mechanical impurities in the water with different backgrounds - mineral, mineral-organic or organic.

The most reliable method for determining the quantity of sludge is filtering through a filter of appropriate porosity and weight determination of the amount of retained substances from the filter.

Indirectly (not exactly), but faster the sludge is carried out on turbidity indicator (transparency) of water.

Sediments of the samples from the Danube defined weighting method and indicator "turbidity".

The test results are object to the protocols No.601 – 610 and the chemical characteristics obtained are presented in the following table 1:

Table 1

Crt no.	**Date**	**Km**	**Protocol no.**	**Turbidity [mg/l]**	**Sediments [%]**	**pH [%]**	**Solids [mg/l]**	**Petrol [mg/l]**
1	19.05.2011	374,5	601	52,9	1,85-2,15	7,18	1630	<0,5
2	19.05.2011	376	602	95,8	2,15-3,10	7,25	1996	<0,5
3	19.05.2011	376	603	74,3	1,15-2,0	7,22	978	<0,5
4	19.05.2011	377	604	86,9	1,75-2,45	6,88	1537	<0,5
5	26.05.2011	505	505	97,5	2,35-3,28	8,12	2976	<0,5
6	26.05.2011	503	606	112,3	3,82-4,25	7,65	3739	<0,5
7	26.05.2011	496	607	87,3	1,15-2,3	7,78	1735	<0,8
8	28.05.2011	488	608	7,6	0,87-1,12	8,25	58,7	<0,7
9	28.05.2011	485	609	38,6	3,25-5,75	8,22	178,3	9,8
10	28.05.2011	484	610	12,7	0,95 – 1,58	8,35	39,7	2,85

Graphically representing (Fig. 3, 4, 5, 6, 7) the leading indicators (turbidity, sediments, pH, solids and oil), as function on which km were done the sampling, in the monitoring period (19.05.2011 – 28.05.2011), we found higher values of oil and solids concentration and proportion of sediments in the Russian region of km 485-488, region where the turbidity recorded the lowest values. pH values are normal ones, between 6,88 and 8,35.

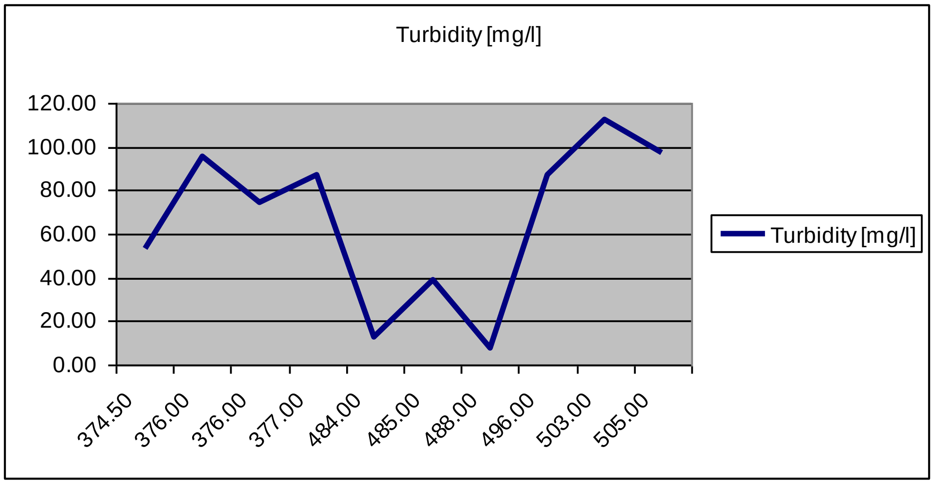


Fig. 3

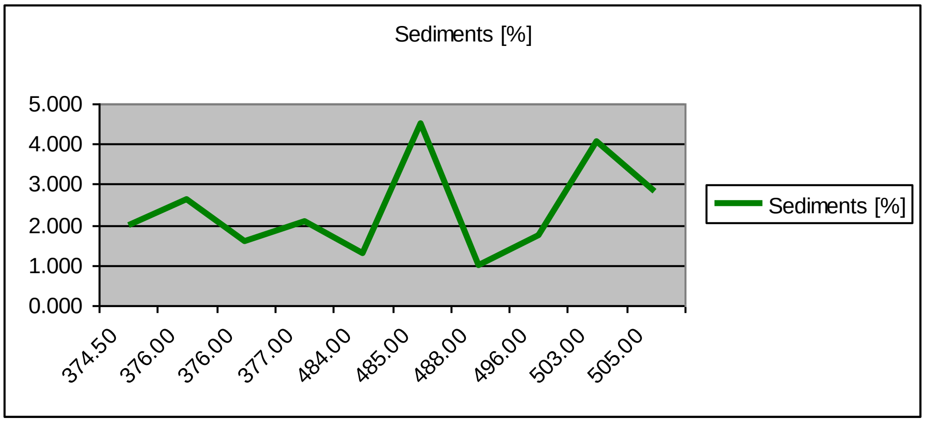


Fig. 4

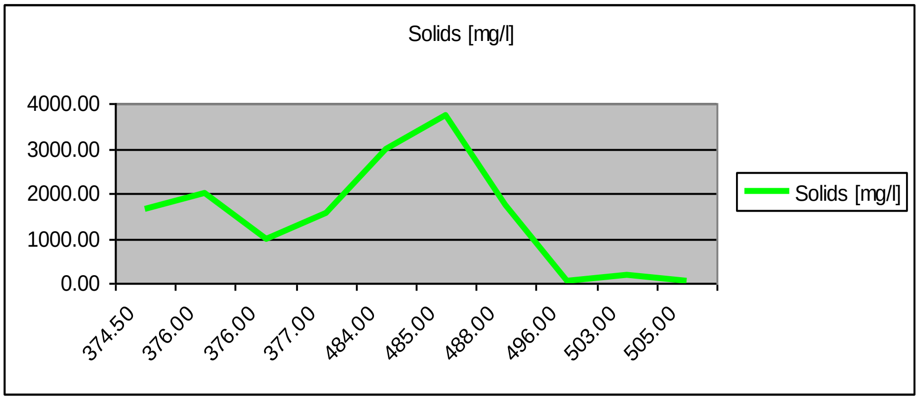


Fig. 5

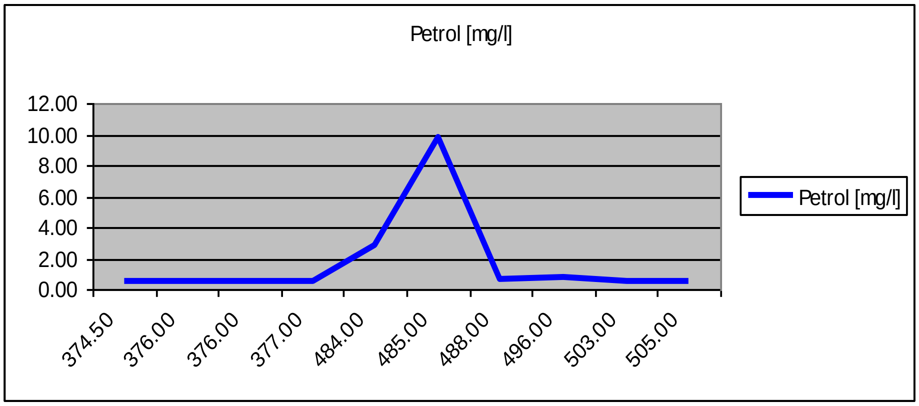


Fig. 6

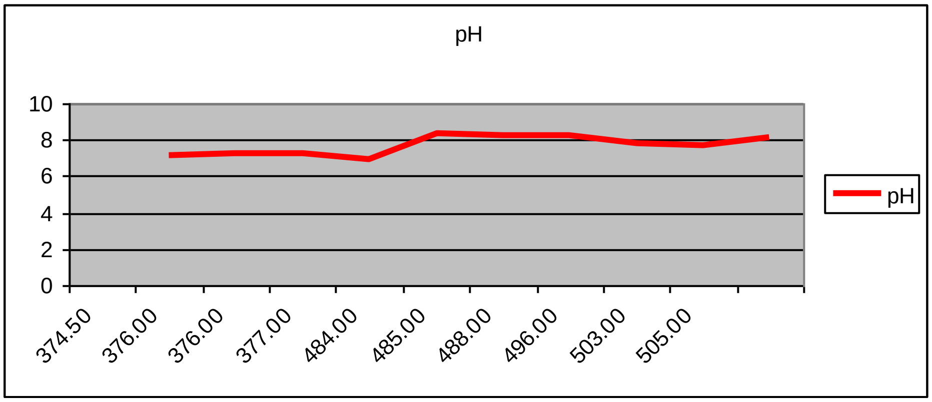
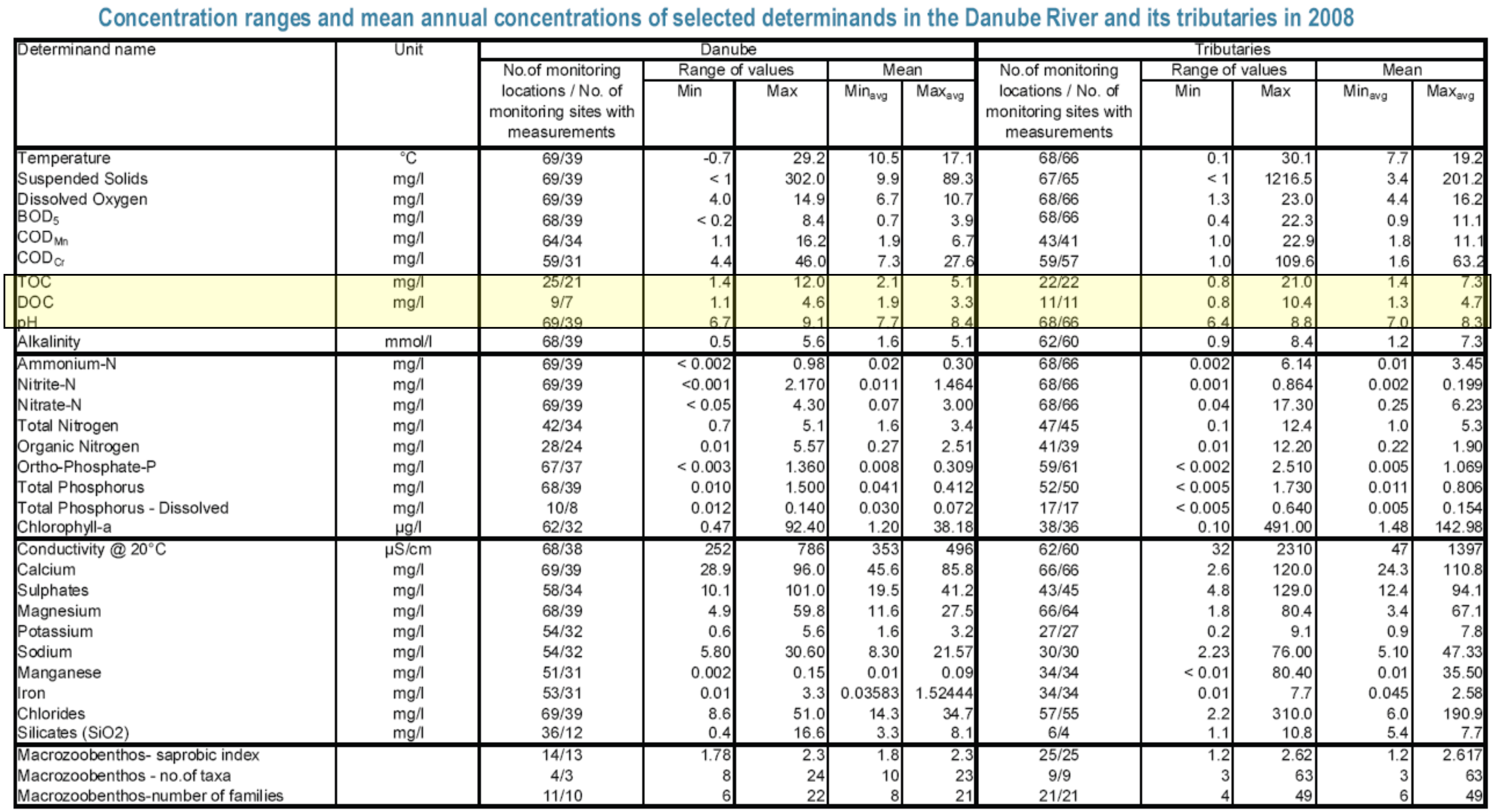


Fig. 7

These values are consistent with average values of TOC (Total organic carbon) and DOC (Disolved organic carbon) from the last official report TNMN - ICPDR (final version 2010), as reflected in the table given below (Fig. 8 - see in yellow underlined) :



Concentration ranges and mean annual concentrations of selected determinands in the Danube River and its tributaries in 2008

Determinand name	Unit	Danube					Tributaries				
		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean		No.of monitoring locations / No. of monitoring sites with measurements	Range of values		Mean	
			Min	Max	Min_{avg}	Max_{avg}		Min	Max	Min_{avg}	Max_{avg}
Temperature	°C	69/39	-0.7	29.2	10.5	17.1	68/66	0.1	30.1	7.7	19.2
Suspended Solids	mg/l	69/39	< 1	302.0	9.9	89.3	67/65	< 1	1216.5	3.4	201.2
Dissolved Oxygen	mg/l	69/39	4.0	14.9	6.7	10.7	68/66	1.3	23.0	4.4	16.2
BOD_5	mg/l	68/39	< 0.2	8.4	0.7	3.9	68/66	0.4	22.3	0.9	11.1
COD_{Mn}	mg/l	64/34	1.1	16.2	1.9	6.7	43/41	1.0	22.9	1.8	11.1
COD_{Cr}	mg/l	59/31	4.4	46.0	7.3	27.6	59/57	1.0	109.6	1.6	63.2
TOC	mg/l	25/21	1.4	12.0	2.1	5.1	22/22	0.8	21.0	1.4	7.3
DOC	mg/l	9/7	1.1	4.6	1.9	3.3	11/11	0.8	10.4	1.3	4.7
pH		69/39	6.7	9.1	7.7	8.4	68/66	6.4	8.8	7.0	8.3
Alkalinity	mmol/l	68/39	0.5	5.6	1.6	5.1	62/60	0.9	8.4	1.2	7.3
Ammonium-N	mg/l	69/39	< 0.002	0.98	0.02	0.30	68/66	0.002	6.14	0.01	3.45
Nitrite-N	mg/l	69/39	<0.001	2.170	0.011	1.464	68/66	0.001	0.864	0.002	0.199
Nitrate-N	mg/l	69/39	< 0.05	4.30	0.07	3.00	68/66	0.04	17.30	0.25	6.23
Total Nitrogen	mg/l	42/34	0.7	5.1	1.6	3.4	47/45	0.1	12.4	1.0	5.3
Organic Nitrogen	mg/l	28/24	0.01	5.57	0.27	2.51	41/39	0.01	12.20	0.22	1.90
Ortho-Phosphate-P	mg/l	67/37	< 0.003	1.360	0.008	0.309	59/61	< 0.002	2.510	0.005	1.069
Total Phosphorus	mg/l	68/39	0.010	1.500	0.041	0.412	52/50	< 0.005	1.730	0.011	0.806
Total Phosphorus - Dissolved	mg/l	10/8	0.012	0.140	0.030	0.072	17/17	< 0.005	0.640	0.005	0.154
Chlorophyll-a	µg/l	62/32	0.47	92.40	1.20	38.18	38/36	0.10	491.00	1.48	142.98
Conductivity @ 20°C	µS/cm	68/38	252	786	353	496	62/60	32	2310	47	1397
Calcium	mg/l	69/39	28.9	96.0	45.6	85.8	66/66	2.6	120.0	24.3	110.8
Sulphates	mg/l	58/34	10.1	101.0	19.5	41.2	43/45	4.8	129.0	12.4	94.1
Magnesium	mg/l	68/39	4.9	59.8	11.6	27.5	66/64	1.8	80.4	3.4	67.1
Potassium	mg/l	54/32	0.6	5.6	1.6	3.2	27/27	0.2	9.1	0.9	7.8
Sodium	mg/l	54/32	5.80	30.60	8.30	21.57	30/30	2.23	76.00	5.10	47.33
Manganese	mg/l	51/31	0.002	0.15	0.01	0.09	34/34	< 0.01	80.40	0.01	35.50
Iron	mg/l	53/31	0.01	3.3	0.03583	1.52444	34/34	0.01	7.7	0.045	2.58
Chlorides	mg/l	69/39	8.6	51.0	14.3	34.7	57/55	2.2	310.0	6.0	190.9
Silicates (SiO2)	mg/l	36/12	0.4	16.6	3.3	8.1	6/4	1.1	10.8	5.4	7.7
Macrozoobenthos- saprobic index		14/13	1.78	2.3	1.8	2.3	25/25	1.2	2.62	1.2	2.617
Macrozoobenthos - no.of taxa		4/3	8	24	10	23	9/9	3	63	3	63
Macrozoobenthos-number of families		11/10	6	22	8	21	21/21	4	49	6	49

Fig. 8

The project will continue with monitoring of these indicators of the Danube River and in the same time with analyzing the possible pollutant petroleum fractions, in order to achieve a realistic design of the separation plant.