Harmful deposits in reciprocating internal combustion engines – methods of assessment and scope of application

Z Stępień and W Krasodomski
Oil and Gas Institute – National Research Institute, Krakow, Poland
stepien@inig.pl

Abstract. The deposits forming on the surfaces of various internal parts of reciprocating internal combustion engines and the systems operating in conjunction with them are an undesirable phenomenon which intensifies during the operation of the engines and threatens their proper operation. More and more complicated engine designs and the increasing accuracy of workmanship of the parts working in conjunction with them necessitate the multi-directional testing of harmful deposits. An increasing number of factors affecting deposit formation are being identified, which leads to the development of increasingly complex classifications and subdivisions of deposits according to their type, composition, and form. The article presents the problems of the deposits produced in reciprocating internal combustion engines and their fuel systems. Standard and non-standard engine and analytical methods for both quantitative and qualitative assessment of deposits are discussed. The significance of currently applied assessment methods for the formation of deposit classification is presented. The paper presents the scope of application and usefulness of methods for the determination of the threats posed by various types of deposits to the functioning of the engine and for the identification of the causes for their formation, including in particular those related to the composition of fuels and engine lubricating oils used. A practical approach to the quantitative and qualitative assessments of deposits is discussed on the examples of engine, microscopic and spectral test assessments of real deposits produced on various elements of SI and CI engines and their fuel systems, including both the fuel supply systems using hydrocarbon fuels and those using fuels containing biocomponents.

1. Introduction
The formation of deposits as a result of processes of fuel injection, the formation of the fuel-air mixture and its combustion in reciprocating combustion engines is a normal phenomenon. The size and composition of the deposits are strongly influenced by the hydrocarbon composition of the conventional fuel, the additive package used, the share and quality of bio-components and the engine lubricating oil that enters the fuel-air mixture and the charge to be burnt. Deposits are formed especially on the surfaces of inlet ducts, inlet valves, fuel injectors and engine combustion chambers. These are mainly organic coke deposits formed as a result of the thermal decomposition of fuel during the combustion process and consisting mainly of carbon and hydrogen but often also containing oxygen, sulfur, nitrogen and other elements. The size of the deposits can be largely controlled by the detergent and dispersant additives added to the fuel [1-7].

It was not until the beginning of the 21st century that extensive multi-directional research began not only to identify the causes of the formation of deposits, the mechanisms of their formation and the factors conducive to deposit growth processes but also to determine the chemical composition of
various groups of deposits. The needs for such research resulted from the requirement of engines to comply with gradually tightening regulations in the area of the environmental protection, which necessitated the introduction of increasingly complex engine designs and strategies for controlling the processes of precise and divided fuel injection into the engine combustion chambers and advanced algorithms for controlling the combustion processes depending on the combustion system and the purpose of the engine. However, it turned out that the co-functioning of the increasingly complex engine technologies and solutions, in particular fuel injection systems, may be significantly disturbed by the deposits formed inside them [4, 8 - 14]. An example of this is the problem of external and internal deposits that form in and interfere with the operation of HPCR (High-Pressure Common Rail) fuel injection systems. Chemical analyses of internal deposits referred to as IDID (Internal Diesel Injector Deposit) have shown that these deposits have a different composition and morphology from external coke deposits formed in the ducts and around the outlets of nozzles [15–17]. The physical nature of the deposits in question may vary, as they may be metal soaps or salts or ashless materials in the form of imide or amide organic polymers, as well as ester deposits of different types [11, 15, 18 - 20].

A completely different group of deposits is the products of degradation of engine lubricating oils. Intensive, thermal, and chemical degradation of lubricating oil causes the formation of oxidation products, which – depending on the temperature – produce various types of deposits in different parts of the engine, which are referred to as low- and high-temperature sludges. These can clog the oil filter, reduce the oil flow in the oil ducts and make it very difficult to spread oil and lubricate engine parts and components. Therefore, it is not a phenomenon occurring during normal use of oil but a sign of a loss of functional properties which leads to emergency wear of parts of engine friction nodes. The conducted tests revealed the complicated nature and a large number of various factors which might affect the above problems, with the main causes, as indicated, being the quality of the lubricating oil and the formulation of the fuel that enters it in combination with the design of the engine and the way in which it is operated and maintained [21 - 24]. Each group of additives making up a multifunctional package of additives used for the improvement of fuel has a different chemical character. In some cases, the use of increasingly complex additive packages can lead to negative interactions both in the fuel and between individual additives or to antagonisms between the additives contained in the fuel and the engine lubricating oil, which can be significantly influenced by the design and the operating conditions of the engine itself. Additionally, the intensification of oil viscosity growth processes, which precede the formation of the sludge, is influenced by the combustion products entering it, including water as a consequence of condensation processes, especially in the conditions of engine operation that causes its frequent heating and cooling, i.e. in the conditions of frequent start-ups and operation of the vehicle in a city over short distances.

The need to examine the deposits described above is often associated with the use of unconventional methods and requires a high degree of creativity and the selection of appropriate tools and methods on each occasion in order to identify the causes of the deposit formation and assess its components [25 - 27]. This was the motivation to discuss standard and non-standard engine tests and analytical methods for both quantitative and qualitative assessment of deposits. The significance of currently applied assessment methods for the formation of deposit classification is presented. A practical approach to the quantitative and qualitative assessments of deposits was discussed on the examples of engine, microscopic and spectral test assessments of real deposits formed on various elements of SI and CI engines and their fuel systems, as well as related to the degradation of the lubricating oil, taking into account the fuel supply systems using hydrocarbon fuels and fuels containing biocomponents.

2. Testing stage

During engine testing, it is possible to obtain test material in the form of samples of different deposits, the analysis of which may be useful or, in many cases, necessary to assess the causes and factors influencing their formation. Such a qualitative assessment of the composition of deposits makes it possible, among other things, to determine its relationship with the composition of the fuel,
the additive package used to improve it or fuel contaminants, and the contribution of engine lubricating oil to their formation. Visual evaluation (e.g. microphotography at a 20-100× magnification) and spectral techniques are normally used for the assessment. Each case requires an individual approach, planning the procedure in advance, and a unique measurement technique based on the visual/microscopic assessment of the deposits.

2.1. Examples of tests of deposits in combustion chambers and on SI engine inlet valves

Below presented is an example of an analysis of the deposits on inlet valves and in combustion chambers of SI engine with an indirect fuel injection system produced in a M102E test according to CEC F-05-93.

The visual and microscopic assessment of the valves (Fig. 1) allowed the identification of the presence of semi-solid organic components in the deposit in addition to highly oxidized substances. Therefore, the deposit was separated into a soluble part in polar organic solvents and a coked part. After removing the fuel residue, a part of the deposits was dissolved with chloroform and the remaining solid was removed mechanically.

![Figure 1](image_url)

**Figure 1.** Pictures of deposits in the engine combustion chamber (A – the chamber with deposits, B – 200x magnification) and on the inlet valve (C – the valve with deposits, D – 200x magnification)

After the solvent evaporation, the obtained deposit removed from the valves was a brown semi-solid substance. Among others, the presence of hydrocarbon bands (3000–2800 cm⁻¹, 1456 cm⁻¹, 1380 cm⁻¹ and 1366 cm⁻¹) and a double band of approx. 1370 cm⁻¹, typical of polyisobutene structures present in many commercial additive packages for engine gasoline, were found in the infrared spectrum (Fig. 2). In addition, we observed a strong band of approx. 1100 cm⁻¹ coming from the vibrations of polyether structures present in detergent additives and carrier oils, standard components of packages for which a typical example is an ethoxylated/propoxylated derivative of dodecylphenol.

The bands in the range from 1800 to 1600 cm⁻¹ can be assigned to products forming in the processes of incomplete combustion (the 1704 cm⁻¹ band is carboxylic structures, the wide band of 1600 cm⁻¹ most probably coming from traces of water present in the structure of hydrated salts of carboxylic acids. For the coked part of the deposits separated from the valves generated in the CEC F-05-93 (M102E) test, which was not washed out with chloroform, spectra of x-ray fluorescence with energy dispersion
(XRF ED) were recorded. It was found that they indicated the presence of significant amounts of zinc, sulfur, calcium, and phosphorus – Fig. 3. These elements are typical elements present in the additive packages and come from the lubricating oil used during the engine lubrication test. In addition, small amounts of elements originating from the wear and tear of engine parts, i.e. iron, copper, and lead, were observed. In addition, the visible chlorine is most likely associated with the use of chloroform as a solvent to wash out the deposits from valves and combustion chambers.

In the case of the deposits washed out from the combustion chambers of this engine, spectra of a similar structure were obtained (Fig. 2 and 3).

To sum up, it was found that in the described case, the components resulting from the degradation of engine lubricating oil and from the processes of wear and tear of engine parts had accumulated in the coked part of the deposit, while the semi-solid part of the deposit was made up to a large extent of the components of the additive package used for gasoline.

![Figure 2](image1.png)

**Figure 2.** Infrared spectrum – FTIR-ATR of deposits from combustion chambers (red line) and inlet valves (green line) of the SI engine with an indirect fuel injection system

![Figure 3](image2.png)

**Figure 3.** Spectra of x-ray fluorescence of deposits from combustion chambers (A) and inlet valves (B) of an SI engine with an indirect fuel injection system
2.2. Example tests of deposits in combustion chambers and inlet valves of an FFV SI engine fueled by E20 fuel

The object of the test was E20 fuel composed of hydrocarbon base gasoline which did not contain any oxygen compounds, second-generation bioethanol in the amount of 20% v/v and a package of detergent and dispersant additives containing ADE-2 (N-alkyl benzoxazine derivative hydrogenated in a heterocyclic ring) and DF30 (ethoxylated/propoxylated derivative of dodecylphenol). The deposits produced in combustion chambers and on inlet valves were tested after 100-hour-long test in an FFV SI engine.

The visual evaluation of the engine parts allowed a conclusion that the deposits contained significant amounts of organic semi-solid components.

The aim of the tests of deposits in the combustion chambers and on the inlet valves was, first of all, to assess the chemical nature of the deposits and try to connect the structures present in the deposits with the structures of package components and engine oil components.

Fig. 4 shows FTIR-ATR spectra of components of additives and products of destruction which were sought in the engine deposits produced in the test.

After removing the fuel residue, the deposits were dissolved with toluene and the remaining solid was removed mechanically.

The deposit washed out from the inlet valves using toluene in an ultrasonic bath was a brown semi-solid substance. The presence of hydrocarbon bands (3000–2800 cm\(^{-1}\), 1459 cm\(^{-1}\), and 1375 cm\(^{-1}\)) was found in the infrared spectrum of the deposit. Additionally, strong bands of approx. 1100 cm\(^{-1}\) resulting from vibrations of polyether structures (DF) were observed. The bands in the range of 1700-1600 cm\(^{-1}\) may be connected with the processes of incomplete combustion (the band of approx. 1685 cm\(^{-1}\) – carbonyl structures, the wide band of approx. 1630 cm\(^{-1}\) hydrated salts of carboxylic acids). Additionally, the bands of approx. 1610 cm\(^{-1}\) and 1243 cm\(^{-1}\), which may come from Petrotex DF30, were visible in the spectrum. No bands were identified that would clearly indicate the presence of residues of the active substance ADE-2. Only the band of approx. 1610 cm\(^{-1}\) is similar to the characteristic bands present in the spectrum of the active substance but it is present simultaneously in the DF spectrum, as well – Fig. 5A.

The toluene-washed deposit from the combustion chambers is a black-brown solid. The presence of hydrocarbon bands (3000–2800 cm\(^{-1}\), 1459 cm\(^{-1}\), and 1375 cm\(^{-1}\)) was found in the infrared spectrum of the deposit. Additionally, the bands in the range of 1100–1000 cm\(^{-1}\) were observed, including a strong band of approx. 1075 cm\(^{-1}\) originating from the vibrations of polyether structures (DF) and...
several weaker bands of unknown origin, probably related to the presence of inorganic salts in the deposit. The bands in the range of 1800-1600 cm⁻¹ are connected to the processes of incomplete combustion (1705 cm⁻¹ band – carboxylic structures, very wide band of approx. 1602 cm⁻¹ is crystallization water and/or hydrated salts of carboxylic acids) – Fig. 5B.

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2.3. Examples of tests of external and internal deposits from fuel injectors of a CI engine with a direct fuel injection system

In the next case, external and internal deposits (HSDI) formed on the surface and inside the injectors in the HSDI CI engine were examined (Fig. 6).

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After removing the fuel residue using extraction gasoline, the produced external deposits were washed out with chloroform, while the deposits from the internal parts of the injectors and the needle were washed out with chloroform and then methanol. The external deposits, isolated in the greatest amount, consisted of a phase of a brown tarry solid and coke; the internal deposits washed out with chloroform in the amount of less than five milligrams were the light-yellow grease-like phases, and the internal deposits washed out with methanol, obtained in trace amounts, were uncolored solid phases.

The separated deposits were evaluated using FTIR-ATR spectroscopy and XRF ED x-ray fluorescence techniques.

The visual evaluation of the injectors (Fig. 6) showed that external deposits are strongly burned substances. In the spectra of the examined deposits (Fig. 7), apart from the trace amounts of iron, no typical signals of wear elements, the presence of elements present in the additive package and in the case of internal deposits (Fig. 7B), the presence of strong silicon signal were found.
These observations were confirmed by the analysis of infrared spectra, where 1019 cm⁻¹ and 1086 cm⁻¹ bands typical of organosilicon structures, which do not occur in hydrocarbon fuels and in FAME, were observed.

![Figure 7. XRF spectra of external (A) and internal (B) deposits from an injector](image_url)

The deposit washed out from injectors using chloroform was a brown semi-solid substance. The presence of hydrocarbon bands (3000–2800 cm⁻¹, 1455 cm⁻¹, and 1377 cm⁻¹) was found in the deposit’s infrared spectrum (Fig. 8). Additionally, bands in the range of 1800–1600 cm⁻¹ associated with the processes of incomplete combustion, a 1710–1700 cm⁻¹ band – carboxylic structures, a wide band of approx. 1604 cm⁻¹ hydrated salts of carboxylic acids and a band of 1257 cm⁻¹ C-O bonds in carboxylic groups and a band of 1166 cm⁻¹ originating from the vibrations of C-O bonds of alcohol or ether structures were observed.

In the spectra of the deposits washed out from internal injector parts using chloroform (Fig. 8), apart from the above-mentioned bands typical of organosilicon compounds, the bands of the residue of the evaporated fuel, i.e. hydrocarbon bands, and a 1746 cm⁻¹ ester band were observed. On the other hand, in the spectrum of the part washed out with methanol (Fig. 8), one can see the bands of FAME oligomers or washed-out engine oil components (the band of approx. 1741 cm⁻¹) and oxidation products, carboxylic acids – a band of approx. 1713 cm⁻¹, hydrated salts of carboxylic acids – a wide band of approx. 1650 cm⁻¹, other products of oxidation – bands 1257 cm⁻¹ and 1170 cm⁻¹.

In the case above, the external deposits are formed by coked solid substances partially soluble in chloroform. In addition to the products of incomplete fuel combustion, they also contain products formed during the engine oil combustion process, while the internal deposits are produced by FAME oligomerization products and organosilicon compounds.
Figure 8. The FTIR-ATR spectrum of injector deposits – the deposits washed out with chloroform from the external surface of injectors (purple line), the deposits washed out from internal injector parts using chloroform and washed out from the needle (green line), the deposits washed out from internal injector parts using methanol and washed out from the needle (red line)

2.4. Examples of tests on the low-temperature sludge from the degradation of engine lubricating oil (SI engine)

An intensive chemical degradation of engine lubricating oil leads to the formation of low-temperature sludge, which can clog the oil filter and settle on the components of the valve timing system, and consequently to an engine failure. These deposits are formed as a result of the processes of oxidation and oligomerization of oil components. In the described case, the deposit accumulated on the oil filter was an amorphous solid. Microscopic pictures of the deposit with accompanying oil residues and the deposit on the filter after oil removal are presented below in Fig. 9 and Fig. 10, respectively. In the latter case, one can clearly see its morphology. The deposit is a vitreous body which does not contain coked components.

Figure 9. Microscopic pictures of the deposit from the degraded lubricating oil deposited on an oil filter (20x and 200x magnification)
Figure 10. Microscopic pictures of the deposit from the degraded lubricating oil deposited on an oil filter after the removal of the oil residue (20x and 200x magnification)

Deposits taken from the upper part of the head and from the components of the valve timing system were of a similar character.

The main component of the deposit present on the oil filter and taken from the engine head and the parts of the valve timing system were organic compounds soluble almost completely in chloroform (over 95%). The virtual absence of coke substances indicates a low-temperature process leading to the formation of these deposits. Additionally, it was found that the chloroform-soluble part of the deposit contained ash components – the incineration residue was about 8% and was a white spongy solid. The morphology of incineration residues and its composition (Ca, S, Zn and P were found by XRF method) indicate that the source of the deposits could be the degraded components of the lubricating oil, such as overbased calcium sulfonates and co-precipitated products of transformations of anti-wear additives (Fig. 11).

Infrared spectra (Fig. 12) confirm the similar chemical character of the deposits accumulating on engine parts and the filter-blocking deposits. The bands of approx. 1705 cm⁻¹ indicate oxidation products of a carboxylic acid character, and the rich structure of the bands in the range of 1280–1000 cm⁻¹ indicates the presence of various oxidation/degradation products, including those of salt or sulfone compounds (the clearly visible band of approx. 1150 cm⁻¹ is an indicator of oil sulfonation during operation). The spectrum of the incineration residues is typical of inorganic salts, i.e. sulfates and phosphates.

Figure 11. The ED-XRF spectrum of the deposit taken from the SI engine timing parts
Figure 12. A comparison of infrared spectra (FTIR-ATR) between 2000 cm\(^{-1}\) and 500 cm\(^{-1}\) of the deposit taken from the parts of a valve timing system: after removal of the oil residue (blue line), the incineration residue (purple line), the chloroform-soluble part (green line) and the chloroform-soluble part of the deposit from the filter (red line)

In the described case, the examined deposits are formed as part of the processes of low-temperature oxidation and oligomerization of the engine oil. The soluble part contains the products of degradation of ash additives used in packages for the improvement of engine lubricating oils, such as overbased salts or zinc alkyl dithiophosphates.

3. Summary and conclusions

The article discusses several cases of tests of deposits forming on the surfaces of parts of the inlet system, the combustion chambers and the fuel system of reciprocating combustion engines. Adequate collection of the deposits, their initial assessment and treatment and usually very difficult interpretation of the results are the key to proper planning and obtaining valuable and reliable results. This is a difficult task that requires adequate experience and often creativity, taking into account, for example, the difficulty of sampling or the very small sample amount to be obtained, which precludes the use of many standard composition assessment methods. Classical spectral methods (FTIR, FTIR-ATR, XRF) and microscopic examinations were used in the described test examples. It is also imperative to be able to select and use two or more methods for the assessment of the tested deposits, which allows for their verification, the improvement of their reliability, expansion and easier connection with the factors that caused the formation of the deposits. In the case of infrared tests, it is important to perform the preparation of the samples because of their small amount (especially when testing internal deposits from injectors). In each case, the key element is the correct interpretation of the results and their connection with both the materials used (fuels, oils, and additives) and their possible contaminants and the operating conditions of the engine.

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