Exergy analysis of cement production

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Abstract: In the present paper, cement production in Greece has been examined using the exergy analysis methodology. The major goal of the modern cement and concrete production industry is the minimisation of energy costs and environmental effects. The rational management of raw materials and energy requires analytical decision making tools that will provide the necessary information for the identification of possible improvements in the life cycle of a product. The second law of Thermodynamics allows for the evaluation of the irreversibility and the exergetic performance of a process. The analysis involves assessment of energy and exergy input at each stage of the cement production process. The chemical exergy of the reaction is also calculated and taken into consideration. It is found that 50% of the exergy is being lost even though a big amount of waste heat is being recovered.

Keywords: cement; concrete; exergy analysis


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work deals primarily with the development of atmospheric wind and dispersion/chemistry models. He coordinated several large international research projects and is the author of more than 300 scientific publications, among them more than 80 in peer-reviewed journals. Professor Moussiopoulos is a member of the German Academy of Natural Scientists, Leopoldina and in 2002 he was awarded the Order of Merit of the Federal Republic of Germany.

1 Introduction

Cement constitutes one of the major manufacturing industries in the Greek economy. Greece’s annual cement production exceeds the 14 million tons of which 50% is being exported. The cement quantity used locally results in more than 30 million m³ of concrete.

The work that is presented here has been completed by creating a production model of the Greek cement production plant located in Thessaloniki, Greece, which is owned and operated by the Titan Cement Company (www.titan.gr).

The production of cement is one of the most energy intensive production processes known. This process also emits a lot of CO₂, due to the decomposition of CaCO₃. Cement production accounts for about 8% of total CO₂ emissions from all human activities (IEA GHG R&D, 1999). It is beneficial from both an environmental and an energy point of view to optimise or redesign this process to improve its efficiency.

The energy input to the process is very high, reaching 3.22 GJ/t, making the exergetic analysis of the process essential. The estimated (OECD, 2000) best practice values of 2.9–3.2 GJ/t compares very well with our calculated value. The cost of energy in most cement production units accounts for more than 25% of the total production cost (Khurana et al., 2002; Sector Report on the Cement Industry). The concept of exergy is very useful in measuring the work that must be supplied to the system in order to remove it from the equilibrium state (Exergetic analysis of the agricultural production system). Exergy could also become a measure of the minimum work required to produce goods and could be used to evaluate energy conversion and utilisation for production systems (Costa et al., 2001) and for national economies (Ayres et al., 1996; Wall, 1977).

2 System description

Cement is a fine, granular powder with hydraulic properties. It contains oxides of calcium, silicon, aluminium and iron, which, combined, represent 90% of its weight. The remainder is gypsum with small quantities of magnesium salts, potassium and other elements. When mixed with water, it sets and hardens either in air or under water. The production cycle of cement and concrete consists of the following stages (Figure 1):
Exergy analysis of cement production

- **Raw materials extraction.** The raw materials for cement production are quarried using powerful excavators or explosives.

- **Limestone crushing.** The limestone is crushed by special machinery into pieces usually smaller than 30 millimetres in size.

- **Raw materials storage and pre-homogenisation.** The raw materials (crushed limestone, quartzite, bauxite, iron oxide, gypsum, etc.,) are stored separately by category, and then conveyed to the mill in carefully set and controlled proportions for mixing.

- **Raw materials grinding.** The mills are metal cylinders with a powerful internal metal shielding that contain tons of spherical steel milling parts. As the mill rotates, these steel spheres crush the raw materials into granules, which form what is called raw meal.

- **Raw meal homogenisation and storage.** The raw meal is conveyed to special silos where the homogenisation process is completed.

- **Firing-clinker production.** After homogenisation, the raw meal moves through a system of cyclones called a preheater, undergoing gradual heat treatment at temperatures up to 900°C. Next, rotary kilns are used to roast the material. The kilns are metal cylinders with a length of 50–150 metres and diameter of 3–5 metres, lined with refractory bricks. The rotary action of the kiln and its angle drive the raw meal towards the exit. The temperature rises as high as 1400°C. Due to processes within the kiln, the raw meal is transformed into a granular hard substance called clinker.

- **Clinker grinding to produce cement.** Clinker is the basic ingredient of cement, and it largely determines the quality of the end product. Cement, as a finished product is a very fine powder that requires for its manufacture a mix of clinker, gypsum and certain natural or artificial materials (such as pozzolana), which grant beneficial properties to the cement. The cement mills resemble the raw meal mills. The exact mix of materials is strictly specified and continuously monitored. The type of cement and level of compressive strength – which is the most important characteristic – depend on the chemical composition of the clinker, the duration of the grinding and the presence or absence of various additives.

- **Cement storage.** The cement produced is stored in silos, which are medium-term storage facilities.

- **Distribution–consumption.** The cement is distributed to consumers either in bags, or in bulk, using special silo trucks or ships.

- **Concrete production.** Cement is mixed with water, sand, stones and gravel with the right proportions in order to produce concrete with the desired properties for a given application.

- **Demolition** of concrete made constructions and transportation of rubble for land-filling.
3 Exergy analysis

Quantification of the input and output streams will lead to the numerical specification for the exergetic analysis that is attempted. The inputs (raw materials and energy) and outputs (emissions) for the production of 1 ton of cement (Vasilakis, 2001) are very well illustrated in Figure 2. The input of various fuels is very clearly indicated on the figure and they also include inputs and outputs for the concrete production.
production. The energy input is of different forms. Solid fuels, mainly pet coke, contribute 57.6%, making it the biggest energy source. Liquid fuels, heavy fuel oil and diesel, account for 35.95%, while electricity and propane constitute the other two types of fuel at 6.42 and 0.002% respectively. Part of the heavy fuel oil is used for the preheating of the kilns, while the rest is used for the heating needs of the plant. The diesel is used for the transportation of the raw materials and of the fuels at the plant. Also, electricity is used for the operation of the electronic parts of the plant, such as the carriers, and the propane is used in the clinker production process. The largest energy consumer in the system is the clinker production process, which constitutes 59.6% of the total energy demand. This is an expected result since the clinker temperature is raised to 1450°C. The rest of the energy goes for the operation of the rest of the units in the production plant.

Figure 2  Life cycle inventory of the system for the production of 1 ton cement (Vasilakis, 2001)
3.1 Exergy: work potential of energy

Exergy (also called availability) is defined as "the maximum useful work that could be obtained from the system at a given state in a specified environment." (Cengel and Boles, 1998)

or as "the maximum amount of work that can be obtained from a stream of matter, heat or work as it comes to equilibrium with a reference environment; it is a measure of the potential of a stream to cause change, as a consequence of not being completely stable relative to the reference environment; exergy is not subject to a conservation law, but it is destroyed due to irreversibilities during any process." (van Schijndel et al., 1998)

Exergy could be represented mathematically as (Ayres et al., 1996; Costa et al., 2001; Szargut et al., 1988; Wall, 1977, 1990):

\[ E = U + P_o V + T_o S - \sum \mu_i n_i \]

where \( U \) is the internal energy, \( P \) is the pressure, \( T \) is the temperature, \( S \) is the entropy, \( \mu_i \) is the chemical potential and \( n_i \) the number of moles.

The work potential of the energy contained in a system at a specified state is simply the maximum useful work that can be obtained from the system. The work done in a process depends on the initial state, the final state, and the process path. That is,

\[ \text{Work} = f(\text{initial state, process path, final state}). \]

In an exergy analysis, the initial state is specified, and thus it is not a variable.

The exergies of different materials once given, an exergy balance of the process in study becomes the vehicle in calculating the exergy losses and the exergy efficiencies of the process. The exergy balance could be depicted (Figure 3) in the following equation:

\[ \text{E}_{\text{in}} = \text{E}_{\text{product}} + \text{E}_{\text{losses}} + \text{E}_{\text{waste}}. \]

The exergy losses are mainly made of irreversibilities and the exergy of waste includes the solid and liquid waste, and air emissions.

Figure 3 Exergy balance
The useful exergy is the exergy of the products. This can be calculated from the exergy balance:

\[ E_{\text{product}} = E_{\text{in}} - E_{\text{losses}} - E_{\text{waste}}. \]

The efficiency of the process is then defined as the % of the useful exergy of the total input exergy:

\[ \phi_p = \frac{E_{\text{product}}}{E_{\text{in}}}, \]

where \( \phi_p \) is the exergetic efficiency.

The % of exergy losses, defined as ‘anergy’ could be calculated as:

\[ \phi_l = \frac{E_{\text{losses}}}{E_{\text{in}}}. \]

In the cement production that this work is dealing with there is only one product and the equation could be applied.

### 3.2 Equations used on applying exergy analysis on cement and concrete production

The following basic (final-deriving) equations (Baehr, 1973) were used in order to apply the exergy analysis methodology on the system studied:

- The physical exergy of a given stream is given by the following equation:
  \[ E_{\text{ph}} = h - h_u + T_u \cdot (s - s_u), \]
  if the heat capacity of the stream is known \( C_p(T) \) then the following equation is used:
  \[ E_{\text{ph}} = \int_{T_u}^{T} C_p(T) \, dT - T_u \cdot \int_{T_u}^{T} \frac{C_p(T)}{T} \, dT. \]

- Mixing exergy: the mixing exergy of a gaseous stream where all of its components can be treated as ideal gases is given by the equation (Koroneos et al., 2003):
  \[ E_{\text{mix}} = R \cdot T_0 \cdot \sum y_i \cdot \ln \left( \frac{y_i}{y_{i0}} \right). \]

The mixing exergy of a combustion gas free of combustible components can be given by the following equation (Ayres et al., 1996):

\[ E_{\text{mix}} = R \cdot T_0 \cdot \left[ y_{\text{N}_2} \cdot \ln \left( \frac{y_{\text{N}_2}}{0.7893} \right) + y_{\text{O}_2} \cdot \ln \left( \frac{y_{\text{O}_2}}{0.2099} \right) + y_{\text{CO}_2} \cdot \ln \left( \frac{y_{\text{CO}_2}}{0.000345} \right) + y_{\text{H}_2}\text{O} \cdot \ln \left( \frac{y_{\text{H}_2}\text{O}}{X_0} \right) + \ln(1 + X_0) \right], \]
Chemical exergy: chemical exergy of a substance is the maximal possible useful work that may be produced by process of physical and chemical equilibration of the substance with the ambient. The chemical exergy of substance can be calculated by the following equation:

\[ E_{Ch} = (\mu^0 - \mu^0_0) + R \cdot T_0 \cdot \ln \left( \frac{C}{C_0} \right) \]

The chemical exergies of substances participating in a reaction of type \( M + N \rightarrow P \) are related to the Gibbs free energy of the reaction \( \Delta G^0 \) by the equation:

\[ E_{ChP}^0 - E_{ChM}^0 - E_{ChN}^0 = \Delta G^0 \]

The chemical exergies of substances are tabulated and the chemical exergy of a gaseous stream with \( N \) components is given:

\[ E_{Ch} = \sum E_{Ch_i} \]

- The total exergy of a stream is:
  \[ \hat{E} = E_{ph} + E_{mix} + E_{Ch} \]
- Exergy of heat:
  \[ E_{heat} = \left( 1 - \frac{T_u}{T} \right) \cdot Q \]
- Exergy efficiency:
  \[ \zeta = 1 - \frac{\text{exergy destroyed}}{\text{exergy input}} \]

### 3.3 Chemical exergy of calcination

The following reactions are occurring in the system:

\[ \begin{align*}
  \text{R1} \quad & \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \Delta H_{R1}^0 = 158 \, \text{kJ/mol} \quad \Delta G_{R1}^0 = 135 \, \text{kJ/mol} \\
  \text{R2} \quad & \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \quad \Delta H_{R2}^0 = 99.7 \, \text{kJ/mol} \quad \Delta G_{R2}^0 = 47.2 \, \text{kJ/mol}
\end{align*} \]

The kiln feed is 75% limestone + 25% shale. The chemical composition of limestone and shale is given in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Limestone %</th>
<th>Shale %</th>
<th>Kiln feed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1.0%</td>
<td>52.0%</td>
<td>13.74%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.6%</td>
<td>14.0%</td>
<td>3.95%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2%</td>
<td>5.0%</td>
<td>1.40%</td>
</tr>
<tr>
<td>CaO</td>
<td>53.4%</td>
<td>13.0%</td>
<td>43.31%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.8%</td>
<td>1.5%</td>
<td>0.97%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1%</td>
<td>2.5%</td>
<td>0.70%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1%</td>
<td>1.0%</td>
<td>0.32%</td>
</tr>
<tr>
<td>CO₂ calcination</td>
<td>42.8%</td>
<td>12.0%</td>
<td>35.11%</td>
</tr>
</tbody>
</table>

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The resulted calcination reaction energy requirements for the calcinations process and the calcination exergy accumulation per kg produced clinker are:

\[
\text{Calc. Energy Req.} = \frac{43.1}{100 - 35.11} \cdot \frac{\Delta H_{R1}^0}{\text{MW}_{\text{CaO}}} + 0.97 \cdot \frac{\Delta H_{R2}^0}{\text{MW}_{\text{MgO}}} = 2.217 \cdot 10^3 \frac{\text{kJ}}{\text{kgClink}}
\]

\[
\text{Calc. Exergy Req} = \frac{43.1}{100 - 35.11} \cdot \frac{\Delta G_{R1}^0}{\text{MW}_{\text{CaO}}} + 0.97 \cdot \frac{\Delta G_{R2}^0}{\text{MW}_{\text{MgO}}} = 1.624 \cdot 10^3 \frac{\text{kJ}}{\text{kgClink}}
\]

### 3.4 Chemical exergy of the fuels

The exergy entering the system is the sum of the exergies of Pet-coke, heavy fuel oil (HFO) and propane, which are burned in the clinker production process. The value of propane is not taken into account due to its very low contribution to the system. The composition of Pet-coke and heavy fuel oil is given in Table 2. The composition of heavy fuel does not sum up to 100% because there is also a percentage of water (0.13%) and ash (0.01%).

#### Table 2 Composition of Pet-coke and heavy fuel % mass (Szargut et al., 1988; Wall, 1990)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Carbon (C)</th>
<th>Hydrogen (H)</th>
<th>Oxygen (O)</th>
<th>Nitrogen (N)</th>
<th>Sulphur (S)</th>
<th>Heating value, $\Delta H$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pet-coke</td>
<td>97.5</td>
<td>0.3</td>
<td>0.3</td>
<td>1</td>
<td>0.9</td>
<td>33.2</td>
</tr>
<tr>
<td>Heavy fuel</td>
<td>86.6</td>
<td>12.2</td>
<td>0.13</td>
<td>0.27</td>
<td>0.7</td>
<td>39.5</td>
</tr>
</tbody>
</table>

The chemical exergy of the fuels entering the system is calculated by using the following expressions (Koroneos et al., 2003):

- for the pet-coke fuel:

\[
E_{\text{PETCOKE}}^{\text{ch}} = \Delta H_{\text{PETCOKE}} \cdot \left(1.0437 + 0.1896 \cdot \frac{x_H}{x_C} + 0.0617 \cdot \frac{x_O}{x_C} + 0.0428 \cdot \frac{x_N}{x_C} + 9710 \cdot x_S\right)
\]

- for the HFO:

\[
E_{\text{HFO}}^{\text{ch}} = \Delta H_{\text{HFO}} \cdot \left(1.0401 + 0.1728 \cdot \frac{x_H}{x_C} + 0.0432 \cdot \frac{x_O}{x_C} + 0.2196 \cdot \frac{x_S}{x_C} \left(1 - 2.0628 \cdot \frac{x_H}{x_C}\right)\right)
\]

where: $x_C$, $x_H$, $x_O$, $x_N$, $x_S$ the mass fractions of the elements in the fuel.

The calculations are based on kg of fuel with the formula $C_m H_n N_p O_q S_t$ undergoing the following combustion reaction:

\[
C_m H_n N_p O_q S_t + \frac{2 \cdot (m + t) - q + \frac{n}{2}}{2} O_2 \rightarrow mCO_2 + \frac{n}{2} H_2O_{\text{liq}} + \frac{p}{2} N_2 + tSO_2
\]

where: $m = x_C/12$, $n = x_H/1$, $q = x_O/16$, $p = x_N/14$, $t = x_S/32$. 
The exergy per kg from the combustion of fuel is given by the equation:

$$\Delta G_{\text{FUEL}} = m \cdot E_{\text{CO}_2}^{\text{ch}} + \frac{n}{2} \cdot E_{\text{H}_2\text{O} \text{liq}}^{\text{ch}} + \frac{p}{2} \cdot E_{\text{N}_2}^{\text{ch}} + t \cdot E_{\text{SO}_2}^{\text{ch}} - E_{\text{FUEL}}^{\text{ch}} = \frac{2 \cdot (m + t) - q + \frac{n}{2}}{2} \cdot E_{\text{O}_2}^{\text{ch}}.$$ 

The results are presented in Table 3.

**Table 3 Exergy of fuels**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Specific exergy $kJ/kg$</th>
<th>Consumption $kg/kg$ clinker</th>
<th>Exergy input $kJ/kg$ clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pet-coke</td>
<td>$3.3 \cdot 10^4$</td>
<td>0.096</td>
<td>$3.23 \cdot 10^3$</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>$4.1 \cdot 10^4$</td>
<td>$1.42 \cdot 10^{-4}$</td>
<td>5.8</td>
</tr>
<tr>
<td>Total</td>
<td>N/A</td>
<td>N/A</td>
<td>$3.23 \cdot 10^3$</td>
</tr>
</tbody>
</table>

Taking into account the chemical exergy accumulated in the product, the energy and exergy efficiency of the reaction we end up in the following numeric values:

$$\text{Reaction Exergy Efficiency} = \frac{\text{Chemical Exergy Accumulation}}{\text{Exergy Input}} \cdot 100 = 50.2\%$$

$$\text{Reaction Energy Efficiency} = \frac{\text{Chemical Energy Accumulation}}{\text{Energy Input}} \cdot 100 = 68.8\%$$

### 3.5 Exergy and energy losses

The flow diagram of the clinker production process with all the heat flow processes is very accurately represented in Figure 4. An analysis of the incoming and outgoing streams will lead to the evaluation of the energy and energy values that are utilised in the system.

The input energy and exergy of the various streams of the clinker production process calculated per kg of clinker produced are presented in Table 4.

Based on Table 4, the Sankey energy and exergy diagrams (Wall, 1990) could be constructed. These diagrams (Figures 5 and 6) give an excellent representation of the exergy and enthalpy balances and of the exergy that are either useful for the process or are destroyed. It is shown that 68.5% of the energy is a useful energy to the system. This value represents 50% of the useful exergy with the remaining 50% being exergy losses at the various stages of the system. The biggest losses (30.9%) are due to irreversibilities in the preheating of feed and the cooling of the product. The exhaust gases from the combustion of the fuel account for another 15.1% of the exergy losses.
Figure 4  Clinker production process

![Clinker production process diagram](image)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Flow rate (kg/kg clinker)</th>
<th>Specific heat (kJ/kgK)</th>
<th>Temperature (°C)</th>
<th>Enthalpy (kJ/kg clinker)</th>
<th>Exergy (kJ/kg clinker)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Entering the process</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw feed</td>
<td>1.54</td>
<td>0.9</td>
<td>50</td>
<td>35</td>
<td>1.4</td>
</tr>
<tr>
<td>Ambient air</td>
<td>2.68</td>
<td>1</td>
<td>20</td>
<td>-13</td>
<td>0.1</td>
</tr>
<tr>
<td>Pet-coke</td>
<td>0.096</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Combustion</td>
<td></td>
<td></td>
<td></td>
<td>3.216 \times 10^3</td>
<td>3.228 \times 10^3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td>3.237 \times 10^3</td>
<td>3.229 \times 10^3</td>
</tr>
<tr>
<td><strong>Exiting the process</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clinker</td>
<td>1</td>
<td>0.81</td>
<td>100</td>
<td>60.75</td>
<td>6.56</td>
</tr>
<tr>
<td>Preheater exhaust</td>
<td>1.83</td>
<td>1.07</td>
<td>310</td>
<td>538.7</td>
<td>488.6</td>
</tr>
<tr>
<td>Hot air from cooler</td>
<td>1.48</td>
<td>1</td>
<td>300</td>
<td>414.5</td>
<td>122.1</td>
</tr>
<tr>
<td>Reaction energy</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.217 \times 10^3</td>
<td>1.644 \times 10^3</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td></td>
<td></td>
<td></td>
<td>3.231 \times 10^3</td>
<td>2.241 \times 10^3</td>
</tr>
<tr>
<td>Other losses</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>988</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td>3.237 \times 10^3</td>
<td>3.229 \times 10^3</td>
</tr>
</tbody>
</table>
4 Conclusions

Cement production is a very energy intensive process. Due to the high temperatures required for the reactions to take place the losses are quite big. The numbers that have been calculated with regard to energy and exergy efficiencies, 68 and 50%, respectively, give an excellent representation. The greatest loss of exergy, 30%, is due to irreversibilities in the following stages:
Exergy analysis of cement production

- preheating of raw feed
- cooling of clinker
- combustion of pet coke.

A large portion of exergy loss is due to exhaust gases from the combustion of Pet-Coke, 15%.

On the other hand, the high temperatures and long residence times required for clinker production, create an alkaline environment that is ideal for capturing toxic substances. In this sense kilns could be used as they are very good waste incinerators. Rotary kilns can easily utilise biomass or scrap tyres, which have a low sulphur content, as fuels.

References


Titan Cement Company, www.titan.gr


Nomenclature

c_p \quad \text{Constant pressure specific heat (kJ/kgK)}
h \quad \text{Specific enthalpy (kJ/kg)}
Q \quad \text{Total heat transfer rate (kW)}
s \quad \text{Specific entropy (kJ/kgK)}
T \quad \text{Temperature (°C or K)}
E \quad \text{Total exergy (kJ)}
E_{Ch} \quad \text{Chemical exergy (kJ)}\
\zeta \quad \text{Exergy efficiency}
\mu^0 \quad \text{Chemical potential in relation to standard state (kJ)}
\mu_0^0 \quad \text{Chemical potential of environmental state in relation to standard state (kJ)}
C \quad \text{Concentration of substance in present state}
C_0 \quad \text{Concentration of substance in environmental state}
y_i \quad \text{Mol fraction in the steam}
y_{0i} \quad \text{Mol fraction in the environment}
MW \quad \text{Molecular weight (kg/mol)}
\Delta H_R \quad \text{Reaction energy (kJ/mol)}
\Delta G_R \quad \text{Gibbs free energy of the reaction (kJ/mol)}

Subscripts

u \quad \text{Atmospheric conditions}